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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	05/10/2016	9332776	4585-101 CIP	9733

23448 7590 04/20/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Charles P. Beetz, Erlanger, KY;
ZoomEssence, Inc., Sayreville, NJ
Robert Corbett, Westfield, NJ;
David Salem, Rapid City, SD;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	9	5786017	A	1998-07-28	Blake, A., et al.	
Change(s) applied to document, /T.M./ 4/11/2016	10	RE37860	E	~~1998-07-28~~ 9/2002	Blake, A., et al.	
	11	4962089	A	1990-10-09	Boden, R., et al.	
	12	4539143	A	1985-09-03	Boden, R., et al.	
	13	4677207	A	1987-06-30	Boden, R., et al.	
	14	4950495	A	1990-08-21	Boden, R., et al.	
	15	4568538	A	1986-02-04	Boden, R., et al.	
	16	4983579	A	1991-01-08	Boden, R., et al.	
	17	4883884	A	1989-11-28	Boden, R., et al.	
	18	4515987	A	1985-05-07	Boden, R., et al.	
	19	4422900	A	1983-12-27	Bordelon, K., et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

23448 7590 04/14/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

EXAMINER	
HWU, DAVIS D	

ART UNIT	PAPER NUMBER
3752	

NOTIFICATION DATE	DELIVERY MODE
04/14/2016	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

hip@hultquistip.com

Response to Rule 312 Communication	Application No.	Applicant(s)
	14/606,771	BEETZ ET AL.
	Examiner	**Art Unit**
	Davis Hwu	3752

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address –

1. ☒ The amendment filed on *03 April 2016* under 37 CFR 1.312 has been considered, and has been:

   a) ☒ entered.

   b) ☐ entered as directed to matters of form not affecting the scope of the invention.

   c) ☐ disapproved because the amendment was filed after the payment of the issue fee.
   Any amendment filed after the date the issue fee is paid must be accompanied by a petition under 37 CFR 1.313(c)(1) and the required fee to withdraw the application from issue.

   d) ☐ disapproved. See explanation below.

   e) ☐ entered in part. See explanation below.

/Davis Hwu/
Primary Examiner, Art Unit 3752

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

23448 7590 03/31/2016
Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

TITLE OF INVENTION: METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	06/30/2016

EXAMINER	ART UNIT	CLASS-SUBCLASS
HWU, DAVIS D	3752	239-463000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Hultquist, PLLC
2 Steven J. Hultquist
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: ZOOMESSENCE, INC.

(B) RESIDENCE: (CITY and STATE OR COUNTRY): SAYREVILLE, NEW JERSEY

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
- ☒ Issue Fee
- ☐ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ☐ A check is enclosed.
- ☒ Payment by credit card. ~~Form PTO-2038 is attached.~~
- ☒ The director is hereby authorized to charge ~~the required fee(s),~~ any deficiency, or credits any overpayment, to Deposit Account Number 08-3284 (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ☐ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ☐ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ☐ Applicant changing to regular undiscounted fee status. — NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date April 6, 2016

Typed or printed name Steven J. Hultquist Registration No. 28,021

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Electronic Patent Application Fee Transmittal

Application Number:	14606771
Filing Date:	27-Jan-2015
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Filer:	Steven John Hultquist
Attorney Docket Number:	4585-101 CIP

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Utility Appl Issue Fee	2501	1	480	480

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**480**

Electronic Acknowledgement Receipt	
EFS ID:	25417687
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	06-APR-2016
Filing Date:	27-JAN-2015
Time Stamp:	16:49:17
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$480
RAM confirmation Number	3497
Deposit Account	083284
Authorized User	HULTQUIST, STEVEN J.
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 CFR 1.16 (National application filing, search, and examination fees) Charge any Additional Fees required under 37 CFR 1.17 (Patent application and reexamination processing fees)	

Charge any Additional Fees required under 37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	101CIP_SubIssueFee.pdf	98093 af4d04526ea474e5d2c08f047563b1fe45f88fac	no	1
Warnings:					
Information:					
2	Issue Fee Payment (PTO-85B)	101CIP_FeeTransmittalPartB.pdf	56895 ea3508d77ad58765cbe72ec99f8a45bb78c51721	no	1
Warnings:					
The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30611 1e6a5d2b452ebefb20753fb517992a2413e32207	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	185599		

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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101-CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Examiner:**	**Davis D. Hwu**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**	**Customer No.:**	**23448**

CERTIFICATE OF EFS FILING

I hereby certify that this document is being filed via EFS in the United States Patent and Trademark Office on **April 6, 2016**.
/steven j. hultquist/

SUBMISSION OF ISSUE FEE IN U.S. PATENT APPLICATION NO. 14/606,771

Mail Stop Issue Fee
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

In response to the Notice of Allowance issued on March 31, 2016 in the above-identified U.S. patent application, enclosed and submitted herewith is a completed Issue Fee Transmittal (PTOL-85, Part B), together with the $480.00 issue fee payment for a small entity. Payment of all such applicable fees is being made by online credit card authorization at the time of EFS filing of this Submission and accompanying Issue Fee Transmittal.

Respectfully submitted,

/steven j. hultquist/
Steven J. Hultquist
Reg. No. 28,021
Attorney for Applicant

HULTQUIST IP
P.O. Box 14329
Research Triangle Park, NC 27709
Phone: (919) 419-9350
Fax: (919) 419-9354
Attorney File No.: 4585-101-CIP

Enclosures:
Issue Fee Transmittal [1 pg.]

The USPTO is hereby authorized to charge any deficiency or credit any overpayment of fees properly payable for this document to Deposit Account No. 08-3284

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101-CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Examiner:**	**Davis D. Hwu**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**	**Customer No.:**	**23448**

CERTIFICATE OF EFS FILING

I hereby certify that this document is being filed via EFS in the United States Patent and Trademark Office on **April 3, 2016**.
/steven j. hultquist/

AMENDMENT UNDER 37 CFR 1.312 IN U.S. PATENT APPLICATION NO. 14/606,771

Mail Stop Issue Fee
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

A post-allowance review of the allowed claims subsequent to receipt of the March 31, 2016 Notice of Allowance in the above-identified application has been conducted, and a same minor amendment is being made herein in each of dependent claims 16-18 under independent claim 10, so that the wording in such dependent claims 16-18 is fully conformed with the antecedent wording of allowed independent claim 10.

Please amend claims 16-18 as set out in **Section I (Amendments to the Claims)** hereof.

Remarks concerning the amendments of claims 16-18 are set out in **Section II (Remarks)** hereof.

Section I (Amendment of the Claims)

Amend claims 16-18 of the application as set out below.

1. **(Original)** A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained;

the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry; and

a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

2. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a food composition.

3. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a flavor composition.

4. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a fragrance composition.

5. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a medicament composition.

6. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a pigment composition.

7. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 3% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

8. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 2% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

9. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 1% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

10. **(Original)** A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of active ingredient encapsulated within a carrier, wherein:

the active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

a weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 5% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

11. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a food composition.

12. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a flavor composition.

13. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a fragrance composition.

14. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a medicament composition.

15. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a pigment composition.

16. **(Currently amended)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 3% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

17. **(Currently amended)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 2% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

18. **(Currently amended)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 1% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

19. **(Original)** The spray dried powder of claim 10, wherein the carrier comprises starch.

20. **(Original)** A spray dried fiber composition, comprising:

a plurality of dried fibers, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry, and wherein the spray dried fiber composition has at least one of the characteristics of (i) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient, and (ii) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient does not vary by more than about 5% during aging of the dried fibers during any period of elevated temperature of about 95°F up to about 1000 hours.

Section II (Remarks)

Claims 16-18 have been amended herein, to insert the word "powder" after the word "dried" in line 3 of each of such claims, so that the wording in such dependent claims 16-18 is fully conformed with the wording ("aging of the dried powder") of allowed independent claim 10, from which each of the claims 16-18 depends.

The amendments in dependent claims 16-18 are made herein to conform the relevant phrase in each of such dependent claims with the same wording ("aging of the dried powder") used in the antecedent recital in allowed independent claim 10.

Accordingly, no new matter (35 USC 132) is introduced by such amendments of dependent claims 16-18, and no new search or consideration is required by the entry of the amendments presented herein.

Entry of this amendment therefore is proper under the provisions of 37 CFR 1.312.

Respectfully submitted,

/steven j. hultquist/
Steven J. Hultquist
Reg. No. 28,021
Attorney for Applicant

HULTQUIST IP
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Research Triangle Park, NC 27709
Phone: (919) 419-9350
Fax: (919) 419-9354

Electronic Acknowledgement Receipt

EFS ID:	25381372
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	03-APR-2016
Filing Date:	27-JAN-2015
Time Stamp:	15:38:44
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Amendment after Notice of Allowance (Rule 312)	101CIP_312Amendment.pdf	126702 51b0c3aff4e0666e4eb18a7e09856f8c0871a778	no	7

Warnings:	
Information:	

Total Files Size (in bytes):	126702

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450
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NOTICE OF ALLOWANCE AND FEE(S) DUE

23448 7590 03/31/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

EXAMINER
HWU, DAVIS D

ART UNIT	PAPER NUMBER
3752	

DATE MAILED: 03/31/2016

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

TITLE OF INVENTION: METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	06/30/2016

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

23448 7590 03/31/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

TITLE OF INVENTION: METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	06/30/2016

EXAMINER	ART UNIT	CLASS-SUBCLASS
HWU, DAVIS D	3752	239-463000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____

2 _____

3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:

❑ Issue Fee

❑ Publication Fee (No small entity discount permitted)

❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**

❑ A check is enclosed.

❑ Payment by credit card. Form PTO-2038 is attached.

❑ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

❑ Applicant asserting small entity status. See 37 CFR 1.27

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

❑ Applicant changing to regular undiscounted fee status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

23448 7590 03/31/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

EXAMINER	
HWU, DAVIS D	

ART UNIT	PAPER NUMBER
3752	

DATE MAILED: 03/31/2016

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 14/606,771	Applicant(s) BEETZ ET AL.	
	Examiner Davis Hwu	Art Unit 3752	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *the amendment of 3/11/2016*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *1-20*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/Davis Hwu/
Primary Examiner, Art Unit 3752

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14606771	BEETZ ET AL.
	Examiner	Art Unit
	DAVIS HWU	3752

CPC- SEARCHED		
Symbol	Date	Examiner
A61K 38/28, 36/539, 36/487, 47/36	2/9/16	dh

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
424	439, 456	2/9/16	dh

SEARCH NOTES		
Search Notes	Date	Examiner
east	2/9/16	dh
search updated	3/28/16	dh

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
	all of above	3/28/16	dh

	/D.H./ Primary Examiner.Art Unit 3752

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14606771	BEETZ ET AL.
	Examiner	**Art Unit**
	DAVIS HWU	3752

CPC						
Symbol					**Type**	**Version**
A23L		1	/	22016	F	2013-01-01
A61K		9	/	16	I	2013-01-01
A61K		9	/	1652	I	2013-01-01
C11B		9	/	00	I	2013-01-01
A23L		1	/	0029	I	2013-01-01
A23V		2002	/	00	A	2013-01-01
			/			
			/			
			/			
			/			
			/			
			/			
			/			
			/			
			/			

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	20	
/DAVIS HWU/ Primary Examiner.Art Unit 3752	03/28/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	20	3

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14606771	BEETZ ET AL.
	Examiner	Art Unit
	DAVIS HWU	3752

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED					
424	439	A	6	1	K	47 / 00 (2006.01.01)						
CROSS REFERENCE(S)												
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)											
424	456											

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	20	
/DAVIS HWU/ Primary Examiner.Art Unit 3752	03/28/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	20	3

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14606771	BEETZ ET AL.
	Examiner	**Art Unit**
	DAVIS HWU	3752

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 20	
/DAVIS HWU/ Primary Examiner.Art Unit 3752 (Primary Examiner)	03/28/2016 (Date)	O.G. Print Claim(s) 20	O.G. Print Figure 3

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP

CONFIRMATION NO. 9733

POA ACCEPTANCE LETTER

23448
Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

OC000000081342385

Date Mailed: 03/11/2016

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 02/29/2016.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/agizaw/

Doc Code: DIST.E.FILE **Document Description: Electronic Terminal Disclaimer - Filed**	PTO/SB/26 U.S. Patent and Trademark Office Department of Commerce

Electronic Petition Request	**TERMINAL DISCLAIMER TO OBVIATE A DOUBLE PATENTING REJECTION OVER A "PRIOR" PATENT**
Application Number	14606771
Filing Date	27-Jan-2015
First Named Inventor	Charles Beetz
Attorney Docket Number	4585-101 CIP
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

☒ Filing of terminal disclaimer does not obviate requirement for response under 37 CFR 1.111 to outstanding Office Action

☒ This electronic Terminal Disclaimer is not being used for a Joint Research Agreement.

Owner	Percent Interest
ZOOMESSENCE, INC.	100%

The owner(s) with percent interest listed above in the instant application hereby disclaims, except as provided below, the terminal part of the statutory term of any patent granted on the instant application which would extend beyond the expiration date of the full statutory term of prior patent number(s)

8939388

as the term of said prior patent is presently shortened by any terminal disclaimer. The owner hereby agrees that any patent so granted on the instant application shall be enforceable only for and during such period that it and the prior patent are commonly owned. This agreement runs with any patent granted on the instant application and is binding upon the grantee, its successors or assigns.

In making the above disclaimer, the owner does not disclaim the terminal part of the term of any patent granted on the instant application that would extend to the expiration date of the full statutory term of the prior patent, "as the term of said prior patent is presently shortened by any terminal disclaimer," in the event that said prior patent later:
- expires for failure to pay a maintenance fee;
- is held unenforceable;
- is found invalid by a court of competent jurisdiction;
- is statutorily disclaimed in whole or terminally disclaimed under 37 CFR 1.321;
- has all claims canceled by a reexamination certificate;
- is reissued; or
- is in any manner terminated prior to the expiration of its full statutory term as presently shortened by any terminal disclaimer.

◉ Terminal disclaimer fee under 37 CFR 1.20(d) is included with Electronic Terminal Disclaimer request.

○ I certify, in accordance with 37 CFR 1.4(d)(4), that the terminal disclaimer fee under 37 CFR 1.20(d) required for this terminal disclaimer has already been paid in the above-identified application.	

Applicant claims the following fee status:

◉ Small Entity

○ Micro Entity

○ Regular Undiscounted

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES

I certify, in accordance with 37 CFR 1.4(d)(4) that I am:

◉ An attorney or agent registered to practice before the Patent and Trademark Office who is of record in this application

Registration Number 28021

○ A sole inventor

○ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application

○ A joint inventor; all of whom are signing this request

Signature	/steven j. hultquist/
Name	Steven Hultquist

*Statement under 37 CFR 3.73(b) is required if terminal disclaimer is signed by the assignee (owner).
Form PTO/SB/96 may be used for making this certification. See MPEP § 324.

Electronic Patent Application Fee Transmittal

Application Number:	14606771
Filing Date:	27-Jan-2015
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Filer:	Steven John Hultquist
Attorney Docket Number:	4585-101 CIP

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Statutory or Terminal Disclaimer	2814	1	160	160
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**160**

Doc Code: DISQ.E.FILE
Document Description: Electronic Terminal Disclaimer – Approved

Application No.: 14606771

Filing Date: 27-Jan-2015

Applicant/Patent under Reexamination: Beetz et al.

Electronic Terminal Disclaimer filed on March 11, 2016

☒ APPROVED

This patent is subject to a terminal disclaimer

☐ DISAPPROVED

Approved/Disapproved by: Electronic Terminal Disclaimer automatically approved by EFS-Web

U.S. Patent and Trademark Office

Electronic Acknowledgement Receipt	
EFS ID:	25167943
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	11-MAR-2016
Filing Date:	27-JAN-2015
Time Stamp:	10:02:16
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$160
RAM confirmation Number	7371
Deposit Account	083284
Authorized User	HULTQUIST, STEVEN J.
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 CFR 1.16 (National application filing, search, and examination fees) Charge any Additional Fees required under 37 CFR 1.17 (Patent application and reexamination processing fees)	

Charge any Additional Fees required under 37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Electronic Terminal Disclaimer-Filed	eTerminal-Disclaimer.pdf	33525 235d46da9a37a3060c24dbbdf34296450b255b0f	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30499 0d5f94d75045a77458e5a158e559f691967b8fee	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	64024		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101-CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Examiner:**	**Davis D. Hwu**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**	**Customer No.:**	**23448**

CERTIFICATE OF EFS FILING

I hereby certify that this document is being filed via EFS in the United States Patent and Trademark Office on **March 11, 2016**.
/steven j. hultquist/

RESPONSE TO FEBRUARY 17, 2016 OFFICE ACTION IN U.S. PATENT APPLICATION NO. 14/606,771

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

This responds to the February 17, 2016 Office Action in the above-identified application.

A listing of the claims of the above-identified patent application is set out in **Section I (Amendments to the Claims)** hereof. No amendments are being made herein.

Remarks concerning the patentable distinction of the pending claims and the substance of the February 17, 2016 Office Action are set out in **Section II (Remarks)** hereof.

Section I (Listing of the Claims)

A listing of the claims 1-20 of the application is set out below. No amendments are being made in this response.

1. **(Original)** A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained;

the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry; and

a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

2. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a food composition.

3. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a flavor composition.

4. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a fragrance composition.

5. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a medicament composition.

6. **(Original)** The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a pigment composition.

7. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 3% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

8. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 2% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

9. **(Original)** The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 1% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

10. **(Original)** A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of active ingredient encapsulated within a carrier, wherein:

the active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

a weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 5% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

11. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a food composition.

12. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a flavor composition.

13. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a fragrance composition.

14. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a medicament composition.

15. **(Original)** The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a pigment composition.

16. **(Original)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 3% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

17. **(Original)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 2% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

18. **(Original)** The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 1% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

19. **(Original)** The spray dried powder of claim 10, wherein the carrier comprises starch.

20. **(Original)** A spray dried fiber composition, comprising:

a plurality of dried fibers, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry, and wherein the spray dried fiber composition has at least one of the characteristics of (i) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient, and (ii) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient does not vary by more than about 5% during aging of the dried fibers during any period of elevated temperature of about 95°F up to about 1000 hours.

Section II (Remarks)

Filing of Terminal Disclaimer to Overcome Nonstatutory Double Patenting Rejection

In response to the nonstatutory double patenting rejection of claims 1-20 over claims 1-31 of U.S. Patent 8,939,388, an eTerminal Disclaimer has concurrently been filed herewith, and granted by the USPTO, terminally disclaiming over such U.S. Patent 8,939,388. Accordingly, it is requested that the nonstatutory double patenting rejection be withdrawn.

Rejection of Claims 1-9 Under Pre-AIA 35 USC 103(a)

In the February 17, 2016 Office Action, claims 1-9 were rejected under pre-AIA 35 USC 103(a) over Jennings U.S. Patent 5,723,424 ("Jennings"). Such rejection is traversed, and reconsideration of the patentability of claims 1-9 is requested, in light of the ensuing remarks.

Claim 1, from which each of the remaining rejected claims 2-9 is directly dependent, is set out below for ease of reference.

> **1. (Original)** A spray dried powder, comprising:
>
> a plurality of **dried particles**, which individually contain an amount of **final active ingredient encapsulated within a carrier resulting from drying a slurry** containing an initial active ingredient, a liquid solvent and the carrier, wherein:
>
> the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained;
>
> **the final active ingredient includes one or more of the constituent components corresponding with those**

> **of the initial active ingredient as modified by the drying of the slurry**; and
>
> a weight percentage of at least one of the **one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient**.
>
> (emphasis added)

Claim 1 specifies a spray dried powder in which an active ingredient is encapsulated in a carrier.

The active ingredient includes one or more constituent components.

At least one of these components is **of a molecular type for obtaining a food, flavor, fragrance, medicament, and/or pigment**, and is **present in the active ingredient in the spray dried powder** (the active ingredient in the spray dried powder being specified as the "final active ingredient") **at a weight percentage that is within about 5% of its weight percentage in the active ingredient prior to spray drying** (the active ingredient prior to spray drying being specified as the "initial active ingredient").

In other words, the spray dried powder includes a molecular type (food, flavor, fragrance, medicament, and/or pigment) component that is **essentially unchanged in weight from its raw ingredient state** (being within about 5% of its weight percentage in the active ingredient prior to spray drying). This is in contrast to conventional spray dried food, flavor, fragrance, medicament and/or pigment active ingredient components, which as a result of the spray drying operation undergo **substantial weight loss due to degradation and decomposition of such active ingredient components, with associated deterioration of flavor, appearance, stability, shelf-life, etc.**

The examiner's attention in this respect is directed to the following passages in the present application, at paragraphs [0010], [0011], [0070], and [0071] thereof:

> [0010] **One of the prominent attributes of the traditional**

spray drying process is the high temperature of the inlet gas (typically on the order of 200 °C) leaving the heater 11 and entering the drying chamber 7, as well as the temperature of the outlet gas exiting the drying chamber 7, which is usually in excess of 100 °C. Although the liquid droplets 8 are injected into the high temperature environment within the chamber 7, the droplets 8 do not actually reach the inlet gas temperature. The droplets 8, however, do become heated to a point at which **considerable portions of desired constituents of the droplets (i.e., portions of the load) are undesirably modified, such as evaporated and/or oxidized**. The undesirable modification to the load (load loss) leads to a **reduction in flavor (in the case of food loads), a reduction in aroma (in the case of fragrances)**, etc. Essentially, evaporation and heat degradation of the load lowers the performance characteristics of the final powder product, and therefore results in a **significant degradation of performance in commercial use and a significant loss of revenue**.

[0011] The above disadvantageous characteristics of the conventional spray dry process have resulted in many process modifications and emulsion formulations to compensate for heat induced alterations in the load. This is especially true in the **pharmaceutical industry, where excessive heating during spray drying leads to degradation of the active ingredient in a powdered medicament**. This also presents a challenge to flavorists in the powdered flavor industry to design flavor formulations that can survive the drying process and deliver acceptable (although significantly flawed) flavor characteristics.

...

[0070] Reference is now made to FIG. 11, which is a graph illustrating the **weight percentage of the desired component(s) within dried powder particles produced using the system of FIG. 2 as compared with the conventional spray drying process**. The no-heat process has demonstrated **higher levels of preservation of starting active ingredients such as volatile flavor molecules**. FIG. 11 shows the results of a 1000 hour accelerated aging study (at elevated temperatures of about 95 °F) comparing powders produced by conventional spray dry processing and the no-heat process. In the illustrated results, amounts of a particular constituent component, in this case a principle molecular type called D-Limonene (obtained from orange oil), were measured in an un-processed source of flavor oil 400, dried powder 402 produced in accordance with the no-heat process described herein, and dried powder 404 produced in accordance with the prior art heated air process. As FIG. 11 clearly shows, the no-heat powder 402 **retains essentially the same flavor oil composition as the original oil source 400**

> **used to produce the starting slurry, whereas the conventionally spray dried powder 404 departs significantly from the original starting oil 400**. Similar results were found for all other principal constituents of other flavor oils. Additionally, the **appearance of degradation products was greatly diminished** in the no-heat samples, resulting in **longer projected shelf-life** of the powder.
>
> [0071] The above data reveal that not only are some of the structures and processes of the system 100 of FIG. 2 inventive, but **the dried powder (or fiber) itself is inventive**. Indeed, the resultant dried powder (or fiber) includes a plurality of dried particles/fibers, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying the slurry, which contained an initial active ingredient, a liquid solvent and the carrier. The initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, bacteria, probiotic, pigment, etc. is obtained. The final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry. **A weight percentage of at least one of the one or more principle molecular types in the final active ingredient is essentially the same (e.g., within about 5%, 4%, 3%, or 1% of a) weight percentage of the corresponding principle molecular types in the initial active ingredient**.

It therefore is seen that the spray dried powder of the present claimed invention, as recited in independent claim 1, achieves a **substantial advance in the art**, as a spray dried product that is **essentially unchanged in weight of its active ingredient component(s)**, and therefore is **correspondingly characterized by superior properties that closely match those in the raw material components of the active ingredients that are used for the spray dried powder**, as compared to spray dried powders of the prior art, which suffer substantial decomposition, degradation, deterioration, and weight loss in the spray drying manufacturing operation.

The cited Jennings reference describes a two-component concrete cleaning mixture.

The first component of the Jennings concrete cleaning mixture includes (i) granular all-purpose clay material ("known under the TM of 'OIL DRI'"- column 1, lines 62-63 of

Jennings) and (ii) granular attapulgite-type clay ("a cat litter of the attapulgite-type clay"- column 1, lines 64-65 of Jennings). Jennings states at column 2, line 1 that the cat litter "has a whitening effect."

The second component of the Jennings concrete cleaning mixture includes (i) powdered Kaolin clay and (ii) powdered, finely ground clay dust. Jennings states at column 2, line 48 that "Kaolin has a high whitening effect."

In use, the first component (OIL DRI + cat litter) of the Jennings two-component mixture is rubbed into the concrete to remove oil and grease from the surface, and then the second component (powdered Kaolin clay + powdered, finely ground clay dust) is spread onto the concrete surface to complete the cleaning action and whiten the formerly soiled concrete as a result of the whitening effect produced by the Kaolin clay.

The Jennings (OIL DRI + cat litter)/(Kaolin + clay dust) composition is not equivalent to or in any way suggestive of the spray dried powder of the present invention. Jennings has been applied on the basis that the Kaolin ingredient "has a whitening effect, column 2, line 48" and therefore "is a pigment" (Office Action, page 2), and that "Jennings discloses a powder comprising: an initial active ingredient and a final active ingredient wherein the ratio of the two ingredients is 50% to 50%" (Office Action, page 2, having reference to the disclosure at column 2, lines 51-52 that "Kaolin can be present at 90% to 50% as an ingredient in the second component [Kaolin + clay dust]...a ratio of 50% to 50% is preferred [in other words 50% Kaolin + 50% clay dust]").

It will be appreciated from the foregoing that the 50% to 50% ratio that has been cited in the Jennings disclosure is simply the relationship of the proportions of Kaolin and clay dust in the powder mixture of such materials - the powder mixture is simply a 50/50 mixture of Kaolin and clay dust, with both Kaolin and clay dust materials being present in the mixture at the same time.

It therefore is correspondingly appreciated that Jennings fails to provide any disclosure or suggestion of the spray dried powder of the applicant's invention.

Jennings, first and foremost, lacks disclosure of any "**spray dried powder**" as recited in applicant's claim 1. The powder disclosed in Jennings is simply a mixture of Kaolin powder and clay dust powder.

Accordingly, Jennings contains no disclosure of, and no basis for deriving, "**particles, which individually contain an amount of final active ingredient encapsulated within a carrier**" as recited in applicant's claim 1.

Further, Jennings contains no disclosure of, and no basis for deriving, a powder in which "**the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry**" as recited in applicant's claim 1.

Still further, Jennings contains no disclosure of, and no basis for deriving, a powder in which "**a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient**" as recited in applicant's claim 1. As pointed out above, the ratio of 50% to 50% in Jennings is simply the ratio of the Kaolin (50% of the total powder) to the clay dust (50% of the total powder), with both being present at the same time with one another.

Jennings does not contain even a single mention of "encapsulation", "encapsulating", or "encapsulated" material. Jennings in fact contains no disclosure whatsoever from which "**particles…of final active ingredient encapsulated within a carrier**" could be inferred, extrapolated, or even hypothesized.

Since Jennings fails to provide any disclosure from which the spray dried powder of applicant's claim 1 can be derived, claim 1 patentably distinguishes over Jennings. It

correspondingly is requested that the rejection of claim 1 based on Jennings be withdrawn.

For at least the same reasons, claims 2-9, each of which depends directly from claim 1, is likewise patentable over Jennings.[1]

Based on all of the foregoing, it is requested that the rejection of claims 1-9 based on Jennings be withdrawn, and that the nonstatutory obviousness-type double patenting rejection of claims 1-20 be withdrawn in view of the eTerminal Disclaimer filed concurrently herewith.

The examiner therefore is respectfully requested to issue a Notice of Allowance for the application.

Respectfully submitted,

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[1] *See* MPEP 2143.03 ("If an independent claim is nonobvious under 35 U.S.C. 103, then any claim depending therefrom is nonobvious. *In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988)").

Electronic Acknowledgement Receipt

EFS ID:	25168228
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	11-MAR-2016
Filing Date:	27-JAN-2015
Time Stamp:	10:07:38
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Amendment/Req. Reconsideration-After Non-Final Reject	101CIP_Response021716OfficeAction.pdf	173895 34b5806e1c5e05da6775758eaaf8d60143accf2f	no	12

Warnings:	
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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/606,771	Filing Date 01/27/2015	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT 03/11/2016	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 20	Minus	** 20	= 0	X $40 =	0
Independent (37 CFR 1.16(h))	* 3	Minus	***3	= 0	X $210 =	0
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	**0**

AMENDMENT	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/KAREN VESTAL/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	14/606,771
Filing Date	1/27/2015
First Named Inventor	Beetz et al.
Title	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
Art Unit	3752
Examiner Name	Davis D. Hwu
Attorney Docket Number	4585-101-CIP

SIGNATURE of Applicant or Patent Practitioner

Signature	/steven j. hultquist/	Date	February 29, 2016
Name	Steven J. Hultquist	Registration Number	28021
Title (if Applicant is a juristic entity)			
Applicant Name (if Applicant is a juristic entity)			

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

[X] *Total of 1 forms are submitted.

PTO/AIA/96 (08-12)
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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: ZOOMESSENCE, INC.

Application No./Patent No.: 14/606,771 Filed/Issue Date: January 27, 2015

Titled: METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

ZOOMESSENCE, INC., a corporation
(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. [X] The assignee of the entire right, title, and interest.

2. [ ] An assignee of less than the entire right, title and interest (check applicable box):

   [ ] The extent (by percentage) of its ownership interest is _____ %. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   [ ] There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. [ ] The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. [ ] The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. [X] An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in United States Patent and Trademark Office at Reel 035202, Frame 0725, or for which a copy thereof is attached.

B. [ ] A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

   1. From: _____ To: _____
      The document was recorded in the United States Patent and Trademark Office at
      Reel _____, Frame _____, or for which a copy thereof is attached.

   2. From: _____ To: _____
      The document was recorded in the United States Patent and Trademark Office at
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This collection of information is required by 37 CFR 3.73(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**.

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STATEMENT UNDER 37 CFR 3.73(c)

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The document was recorded in the United States Patent and Trademark Office at
Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☐ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/steven j. hultquist/	February 29, 2016
Signature	Date
Steven J. Hultquist	28,021
Printed or Typed Name	Title or Registration Number

Electronic Acknowledgement Receipt

EFS ID:	25044447
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	29-FEB-2016
Filing Date:	27-JAN-2015
Time Stamp:	11:11:54
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Miscellaneous Incoming Letter	101CIP_SubmissionPOA_Transmittal_373Statement.pdf	98517 97049d19f85e38bcb781fe15cc3ba3f125971a6b	no	2

Warnings:	
Information:	

2	Power of Attorney	101CIPZoomEssencePOA.pdf	41830 b591e6712e9d1e777ddd4ee03d4299be867a3503	no	1
Warnings:					
Information:					
3	Power of Attorney	101CIP_POATransmitttal.pdf	86306 a511ff0cbf1439fa1e0f83429a448c3d9e09f848	no	1
Warnings:					
Information:					
4	Assignee showing of ownership per 37 CFR 3.73	101CIP_373Statement.pdf	138784 04990ac05ee5886f7e88ae80903a4e37a01035a5	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	365437	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101 CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Examiner:**	**Davis D. Hwu**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**	**Customer No.:**	**23448**

CERTIFICATE OF EFS FILING

I hereby certify that this document is being filed via EFS in the United States Patent and Trademark Office on **February 29, 2016**.
/steven j. hultquist/

SUBMISSION OF POWER OF ATTORNEY, POWER OF ATTORNEY TRANSMITTAL, AND 3.73(c) STATEMENT, IN U.S. PATENT APPLICATION NO. 14/606,771

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

Enclosed and submitted herewith are a Power of Attorney, a Power of Attorney Transmittal, and a Statement under 37 CFR 3.73(c), for entry in the above-identified patent application. It therefore is requested that power of attorney for the application be recognized in the undersigned attorney and other practitioners associated with Customer Number 23448 for this application.

Respectfully submitted,

/steven j. hultquist/
Steven J. Hultquist
Reg. No. 28,021
Attorney for Applicant

HULTQUIST IP
P.O. Box 14329
RTP, NC 27709
Phone: (919) 419-9350
Fax: (919) 419-9354
Attorney File No.: 4585-101 CIP

The USPTO is hereby authorized to charge any deficiency or credit any overpayment of fees properly payable for this document to Deposit Account No. 08-3284

POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: the boxes may be left blank if information is provided on attached transmittal letter.)

[X] I hereby appoint Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter or identified above:

OR

23448

[ ] I hereby appoint Practitioner(s) named below as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter or identified above:

Name	Registration Number		Name	Registration Number

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or boxes above to:

[X] The address associated with the above-mentioned Customer Number.

OR

[ ] The address associated with Customer Number:

OR

[ ] Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

ZoomEssence, Inc.

[ ] Inventor or Joint Inventor (title not required below)

[ ] Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

[X] Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

[ ] Person Who Otherwise Shows Sufficient Proprietary Interest (*e.g.*, a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	Robert Corbett	Date	2/29/16
Name	Robert Corbett	Telephone	(908) ~~707-4400~~ 902-0547
Title	Chairman and CEO, ZoomEssence, Inc.		

NOTE: Signature – This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

[X] *Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.31, 1.32 and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/606,771	01/27/2015	Charles P. Beetz	4585-101 CIP	9733

23448 7590 02/17/2016

Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

EXAMINER	
HWU, DAVIS D	

ART UNIT	PAPER NUMBER
3752	

NOTIFICATION DATE	DELIVERY MODE
02/17/2016	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

hip@hultquistip.com

Office Action Summary	Application No. 14/606,771	Applicant(s) BEETZ ET AL.	
	Examiner Davis Hwu	Art Unit 3752	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *27 January 2015*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-20* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-20* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date *4/2/2015*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

1. This office action is in response to the application of January 27, 2015.

2. In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

Claim Rejections - 35 USC § 103

3. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

4. Claims 1-9 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Jennings.

Jennings discloses a powder comprising: an initial active ingredient and a final active ingredient wherein the ratio of the two ingredients is 50% to 50%, wherein the initial ingredient is a pigment as recited in claim 6 (has a whitening effect, column 2, line 48). Jennings does not disclose the final ingredient being within about 5% of the initial ingredient, however, a ratio of 50.5% and 49.5% for example between the two ingredients would not affect the function of the product. Jennings does not disclose the method of forming the final active ingredient, however, a comparison of the recited process with the prior art processes does not serve to resolve the issue co patentability

of the product. Whether a product is patentable depends on whether it is known in the art or it is obvious, and is not governed by whether the process by which it is made is patentable. Regarding claims 2-5, the molecular types as recited would have been matters involving the final material to be made and the prior art has already taught a dry powder comprising two ingredients.

Double Patenting

5. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory double patenting rejection is appropriate where the claims at issue are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); In re Vogel, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the reference application or patent either is shown to be commonly owned with this application, or claims an invention made as a result of

activities undertaken within the scope of a joint research agreement. See MPEP § 717.02 for applications subject to examination under the first inventor to file provisions of the AIA as explained in MPEP § 2159. See MPEP §§ 706.02(l)(1) - 706.02(l)(3) for applications not subject to examination under the first inventor to file provisions of the AIA. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO Internet website contains terminal disclaimer forms which may be used. Please visit www.uspto.gov/forms/. The filing date of the application in which the form is filed determines what form (e.g., PTO/SB/25, PTO/SB/26, PTO/AIA/25, or PTO/AIA/26) should be used. A web-based eTerminal Disclaimer may be filled out completely online using web-screens. An eTerminal Disclaimer that meets all requirements is auto-processed and approved immediately upon submission. For more information about eTerminal Disclaimers, refer to http://www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp.

6. Claims 1-20 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-31 of U.S. Patent No. 8,939,388. Although the claims at issue are not identical, they are not patentably distinct from each other because the product is disclosed as being made by the methods of '388.

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Davis Hwu whose telephone number is (571)272-4904. The examiner's supervisor, Len Tran can be reached on (571)272-1184. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300. Information regarding the status of an application may be obtained from the

Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Davis Hwu/
Primary Examiner, Art Unit 3752

Notice of References Cited	Application/Control No. 14/606,771	Applicant(s)/Patent Under Reexamination BEETZ ET AL.	
	Examiner Davis Hwu	Art Unit 3752	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-8,939,388 B1	01-2015	Beetz; Charles P.	F26B3/12	239/690
*	B	US-5,723,424 A	03-1998	Jennings; Paul E.	C11D11/0052	134/42
	C	US-				
	D	US-				
	E	US-				
	F	US-				
	G	US-				
	H	US-				
	I	US-				
	J	US-				
	K	US-				
	L	US-				
	M	US-				

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	14606771
Filing Date	2015-01-27
First Named Inventor	Beetz
Art Unit	3752
Examiner Name	
Attorney Docket Number	4585-101-CIP

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3655397	A	1972-04-11	Parliment, T., et al.	
	2	5153011	A	1992-10-06	Patel, M., et al.	
	3	5462978	A	1995-10-31	Penzel, E., et al.	
	4	4511592	A	1985-04-16	Percel, P., et al.	
	5	6335045	B1	2002-01-01	Peters, L., et al.	
	6	6391361	B1	2002-05-21	Peters, L., et al.	
	7	3963559	A	1976-06-15	Petersen, M., et al.	
	8	7176176	B2	2007-02-13	Pickenhagen, W., et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	9	4490403	A	1984-12-25	Pisecky, J., et al.	
	10	5100509	A	1992-03-31	Pisecky, J., et al.	
	11	3956521	A	1976-05-11	Pisecky, J., et al.	
	12	4141783	A	1979-02-27	Pisecky, J., et al.	
	13	4680142	A	1987-07-14	Pittet, A., et al.	
	14	4794193	A	1988-12-27	Pittet, A., et al.	
	15	4571344	A	1986-02-18	Pittet, A., et al.	
	16	4626440	A	1986-12-02	Pittet, A., et al.	
	17	4613511	A	1986-09-23	Pittet, A., et al.	
	18	4623538	A	1986-11-18	Pittet, A., et al.	
	19	4623547	A	1986-11-18	Pittet, A., et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

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	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	20	4600576	A	1986-07-15	Pittet, A., et al.	
	21	4521613	A	1985-06-04	Pittet, A., et al.	
	22	4565707	A	1986-01-21	Pittet, A., et al.	
	23	4552770	A	1985-11-12	Pittet, A., et al.	
	24	6582728	B1	2003-06-24	Platz, R., et al.	
	25	6769200	B2	2004-08-03	Raehse, W., et al.	
	26	5968575	A	1999-10-19	Rasmussen, C.	
	27	3679416	A	1972-07-25	Reich, I.	
	28	6200949	B1	2001-03-13	Reijmer, H., et al.	
	29	4524010	A	1985-06-18	Reuter, H., et al.	
	30	4302481	A	1981-11-24	Ribnitz, P., et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

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	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	31	6251463	B1	2001-06-26	Rossy, P., et al.	
	32	2954293	A	1960-09-27	Rusoff, I.	
	33	4532145	A	1985-07-30	Saleeb, F., et al.	
	34	4420442	A	1983-12-13	Sands, B.	
	35	7348035	B2	2008-03-25	Schleifenbaum, B., et al.	
	36	6902751	B1	2005-06-07	Schleifenbaum, B., et al.	
	37	4362273	A	1982-12-07	Seino, J., et al.	
	38	4849125	A	1989-07-18	Seiter, W., et al.	
	39	4661281	A	1987-04-28	Seiter, W., et al.	
	40	4476042	A	1984-10-09	Sprecker, M., et al.	
	41	4537704	A	1985-08-27	Sprecker, M., et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	42	4629805	A	1986-12-16	Sprecker, M., et al.	
	43	4614831	A	1986-09-30	Sprecker, M., et al.	
	44	4643903	A	1987-02-17	Sprecker, M., et al.	
	45	4681976	A	1987-07-21	Sprecker, M., et al.	
	46	5891473	A	1999-04-06	Stanier, P.	
	47	6734158	B2	2004-05-11	Starkenmann, C.	
	48	5506353	A	1996-04-09	Subramaniam, A.	
	49	6723359	B2	2004-04-20	Subramaniam, A., et al.	
	50	5702749	A	1997-12-30	Sugiura, M., et al.	

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear

EFS Web 2.1.17 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /D.H./

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] ¡	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		☐

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Examiner Signature	/Davis Hwu/	Date Considered	02/09/2016

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	14606771
Filing Date	2015-01-27
First Named Inventor	Beetz
Art Unit	3752
Examiner Name	
Attorney Docket Number	4585-101-CIP

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4936901	A	1990-06-26	Surgant, J., et al.	
	2	5227017	A	1993-07-13	Tanaka, T., et al.	
	3	5759599	A	1998-06-02	Wampler, D., et al.	
	4	4724121	A	1988-02-09	Weyand, J.	
	5	7332468	B2	2008-02-19	Widder, S., et al.	
	6	4525364	A	1985-06-25	Wiegers, W., et al.	
	7	4522765	A	1985-06-11	Wiegers, W., et al.	
	8	4072570	A	1978-02-07	Williams, W.	

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	9	4539209	A	1985-09-03	Wilson, R., et al.	
	10	4629586	A	1986-12-16	Wilson, R., et al.	
	11	3805869	A	1974-04-23	Winter, H., et al.	
	12	5391647	A	1995-02-21	Yamamoto, N., et al.	
	13	5137741	A	1992-08-11	Zampino, M., et al.	
	14	7090832	B2	2006-08-15	Zanone, J., et al.	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20090110796	A1	2009-04-30	Backes, M., et al.	
	2	20110064783	A1	2011-03-17	Bang-Madsen, B., et al.	
	3	20080008801	A1	2008-01-10	Barnekow, R., et al.	

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	4	20080057175	A1	2008-03-06	Barnekow, R., et al.	
	5	20080107786	A1	2008-05-08	Barnekow, R., et al.	
	6	20070166185	A1	2007-07-19	Bartels, F.	
	7	20080063747	A1	2008-03-13	Boghani, N., et al.	
	8	20050209443	A1	2005-09-22	Bolen, P., et al.	
	9	20030082272	A1	2003-05-01	Bouwmeesters, J., et al.	
	10	20090081140	A1	2009-03-26	Brocke, C., et al.	
	11	20100196493	A1	2010-08-05	Buisson, P.	
	12	20080241322	A1	2008-10-02	Bunge, R	
	13	20070231424	A1	2007-10-04	Castro, A., et al.	
	14	20030003212	A1	2013-01-02	Chien, M., et al.	

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	15	20080199592	A1	2008-08-21	Fexer, W., et al.	
	16	20110059205	A1	2011-03-10	Gaysinsky, S., et al.	
	17	20040253343	A1	2004-12-16	Ha, Y., et al.	
	18	20030196957	A1	2003-10-23	Henningfield, T., et al.	
	19	20140205713	A1	2014-07-24	Hans, K., et al.	
	20	20080064625	A1	2008-03-13	Holscher, B.	
	21	20080081779	A1	2008-04-03	Holscher, B.	
	22	20060264130	A1	2006-11-23	Karles, G., et al.	
	23	20030192815	A1	2003-10-16	Kelly, A.	
	24	20030205629	A1	2003-11-06	Kelly, A.	
	25	20070297993	A1	2007-12-27	Kindel, G., et al.	

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	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	26	20040062845	A1	2004-04-01	Krawczyk, G., et al.	
	27	20060159818	A1	2006-07-20	Kunieda, S.	
	28	20090124701	A1	2009-05-14	Langer, K., et al.	
	29	20090155445	A1	2009-06-18	Le, A., et al.	
	30	20070078071	A1	2007-04-05	Lee, K., et al.	
	31	20090163403	A1	2009-06-25	Levorse, Jr., A., et al.	
	32	20090163404	A1	2009-06-25	Levorse, Jr., A., et al.	
	33	20080113073	A1	2008-05-15	Ley, J., et al.	
	34	20080214675	A1	2008-09-04	Ley, J., et al.	
	35	20080220140	A1	2008-09-11	Ley, J., et al.	
	36	20080227866	A1	2008-09-18	Ley, J., et al.	

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Examiner Signature	/Davis Hwu/	Date Considered	02/09/2016

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☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

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SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14606771	BEETZ ET AL.
	Examiner	Art Unit
	DAVIS HWU	3752

CPC- SEARCHED		
Symbol	Date	Examiner
A61K 38/28, 36/539, 36/487, 47/36	2/9/16	dh

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
424	439, 456	2/9/16	dh

SEARCH NOTES		
Search Notes	Date	Examiner
east	2/9/16	dh

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

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U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4476147	A	1984-10-09	Hall, J., et al.	
	2	4535192	A	1985-08-13	Hall, J., et al.	
	3	4548821	A	1985-10-22	Hall, J., et al.	
	4	4632831	A	1986-12-30	Hall, J.	
	5	6253463	B1	2001-07-03	Hansen, O.	
	6	6497911	B1	2002-12-24	Hansen, O., et al	
	7	7128936	B1	2006-10-31	Hansen, O.	
	8	3966975	A	1976-06-29	Hansen, K., et al.	

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	9	4099982	A	1978-07-11	Hansen, O, et al.	
	10	3920815	A	1975-11-18	Harvey, R., et al.	
	11	4281024	A	1981-07-28	Hauberg, G., et al.	
	12	4438147	A	1984-03-20	Hedrick, Jr., P.	
	13	7204998	B2	2007-04-17	Holzner, G., et al.	
	14	4062641	A	1977-12-13	Hovmand, S., et al.	
	15	5196219	A	1993-03-23	Hsu, C., et al.	
	16	6838100	B2	2005-01-04	Jaeger, D., et al.	
	17	4001437	A	1977-01-04	Jaeggi, K., et al.	
	18	6652898	B2	2003-11-25	Jensen, J.	
	19	5338553	A	1994-08-16	Johnson, D., et al.	

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	20	4070766	A	1978-01-31	Kamphuis, G.	
	21	5130149	A	1992-07-14	Keller, A., et al.	
	22	7651713	B2	2010-01-26	Keller, A.	
	23	6964385	B2	2005-11-15	Kelly, A.	
	24	6656394	B2	2003-12-02	Kelly, A.	
	25	6474573	B1	2002-11-05	Kelly, A.	
	26	5443829	A	1995-08-22	Kensil, C., et al.	
	27	7316826	B2	2008-01-08	Kindel, G., et al.	
	28	5525367	A	1996-06-11	King, C., et al.	
	29	4892910	A	1990-01-09	Klesse, W., et al.	
	30	7176177	B2	2007-02-13	Lambrecht, S., et al.	

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	31	5840360	A	1998-11-24	Larsen, T.	
	32	7378121	B2	2008-05-27	Ley, J., et al.	
	33	4679733	A	1987-07-14	Lipp, C.	
	34	4804496	A	1989-02-14	Lowery, R., et al.	
	35	6933265	B2	2005-08-23	Marty, M.	
	36	3741273	A	1973-06-26	Meade, R.	
	37	3615723	A	1971-10-26	Meade, R., et al.	
	38	4276312	A	1981-06-30	Merritt, C.	
	39	4198308	A	1980-04-15	Micciche, G.	
	40	4873112	A	1989-10-10	Mitchell, C., et al.	
	41	4481221	A	1984-11-06	Mookherjee, B., et al.	

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	42	4840801	A	1989-06-20	Mookherjee, B., et al.	
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	First Named Inventor	Beetz
	Art Unit	3752
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	1	2008113778	WO	A1	2008-09-25	Whitehouse, A.		☐
	2	1106081	EP	A1	2001-06-13	Witteveen, F., et al.		☐
	3	2171389	CA	C	1996-03-08	Yamada, T., et al.		☐
	4	0461197	EP	B1	1994-06-01	Yatka, R., et al.		☐
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	1	LANGRISH, T., ET AL., "Spray drying of food ingredients and applications of CFD in spray drying", "Chemical Engineering and Processing", 2001, Page(s) 345-354, Volume 40	☐

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	6	SIRIGNANO, W., "Fluid Dynamics and Transport of Droplets and Sprays, Second Edition", January 2010, Page(s) 34, Publisher: Cambridge University Press	☐
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	8	NOTE: For the non-patent literature citations that no month of publication is indicated, the year of publication is more than 1 year prior to the effective filing date of the present application.	☐

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A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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	2	4931203	A	1990-06-05	Ahmed, F., et al.	
	3	6058624	A	2000-05-09	Bach, P., et al.	
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	10	RE37860	E	1998-07-28	Blake, A., et al.	
	11	4962089	A	1990-10-09	Boden, R., et al.	
	12	4539143	A	1985-09-03	Boden, R., et al.	
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	43	7252848	B2	2007-08-07	Gelin, J.	
	44	5773061	A	1998-06-30	Getler, J., et al.	
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	1	0420509	EP	A1	1991-04-03	Arora, V., et al.		☐
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	9	1064856	EP	A2	2001-01-03	De Ross, K., et al.		☐
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	12	1162699	CA	A	1984-02-21	Gagliani, J., et al.		☐
	13	0344375	EP	B1	1989-12-06	Haak, M.		☐
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	15	2012122010	WO	A2	2012-09-13	Hans, K., et al.		☐
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	17	2052622	EP	A1	2009-04-29	Hiemstra, M.		☐
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	26	2407614	CA	C	2001-11-08	Mizuguchi, T., et al.		☐
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	31	62024	IE	B1	1994-12-14	Pisecky, J., et al.		☐
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	42	2008047301	WO	A1	2008-04-24	Somerville Roberts, N., et al.		☐
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	9	KILLEEN, M., "The Process of Spray Drying and Spray Congealing", "Pharmaceutical Engineering", July/August 1993, Page(s) 56, 58-62, 64, Volume 13	☐
	10	NOTE: For the non-patent literature citations that no month of publication is indicated, the year of publication is more than 1 year prior to the effective filing date of the present application.	☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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	Attorney Docket Number	4585-101-CIP

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☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

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A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
14/606,771	01/27/2015	239	3752	4585-101 CIP

APPLICANTS
ZoomEssence, Inc., Sayreville, NJ

INVENTORS
Charles P. Beetz, Erlanger, KY;
Robert Corbett, Westfield, NJ;
David Salem, Rapid City, SD;

**** CONTINUING DATA ***************************
This application is a CIP of 13/245,369 09/26/2011 PAT 8939388
which claims benefit of 61/386,762 09/27/2010

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Foreign Priority claimed ☐ Yes ☑ No 35 USC 119(a-d) conditions met ☐ Yes ☐ No Verified and Acknowledged /DAVIS D HWU/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
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Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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	42	4840801	A	1989-06-20	Mookherjee, B., et al.	
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	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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	2	1106081	EP	A1	2001-06-13	Witteveen, F., et al.		☐
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Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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	Attorney Docket Number	4585-101-CIP

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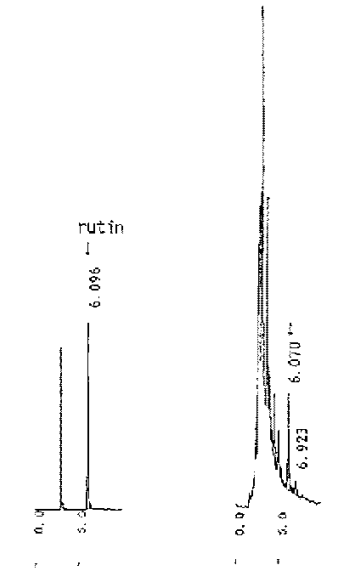
(11) (21) (C) **2,171,389**
(22) 1996/03/08
(43) 1996/09/11
(45) 1998/12/08

(72) Yamada, Takao, JP
(72) Iijima, Yoshio, JP
(73) Sakuma Seika Kabushiki Kaisha, JP

(51) Int.Cl.[6] A23L 1/09, C12S 3/12
(30) 1995/03/10 (51247/1995) JP

(54) **SIROP DE GLUCOSE DE SARRASIN EN POUDRE ET METHODE DE PREPARATION**

(54) **POWDERED BUCKWHEAT STARCH SYRUP AND METHOD FOR PREPARING THE SAME**



HPLC chromatography

(57) La présente invention porte sur un sirop d'amidon de sarrasin en poudre obtenu en liquéfiant l'amidon présent dans la farine de sarrasin et en séchant par atomisation l'amidon liquéfié, ainsi que sur une méthode de préparation correspondante. Le sirop d'amidon de sarrasin en poudre de la présente invention contient divers acides aminés et minéraux, ainsi que de la rutine qui contribue à prévenir l'artériosclérose et, par conséquent, est bonne pour la santé et est équilibrée sur le plan nutritif.

(57) The present invention relates to a powdered buckwheat starch syrup prepared by liquefying starch from buckwheat flour and spray-drying the liquefied starch, as well as a method for preparing the same. The powdered buckwheat starch syrup of the present invention contains various amino acids and minerals, as well as rutin which is effective in preventing arteriosclerosis, and hence it is healthy and excellent in nutritive balance.

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ABSTRACT

The present invention relates to a powdered buckwheat starch syrup prepared by liquefying starch from buckwheat flour and spray-drying the liquefied starch, as well as a method for preparing the same. The powdered buckwheat starch syrup of the present invention contains various amino acids and minerals, as well as rutin which is effective in preventing arteriosclerosis, and hence it is healthy and excellent in nutritive balance.

POWDERED BUCKWHEAT STARCH SYRUP AND METHOD FOR PREPARING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a powdered buckwheat starch syrup prepared by liquefying and spray-drying starch from buckwheat flour, as well as a method for preparing the same.

2. Description of the Prior Art

As raw materials for preparing starch syrups, there have been used various kinds of starch from corn, potato, sweet potato, tapioca, wrinkle-seeded pea, wheat, arrowroot, sago palm, rice, etc. Starch syrups are viscous, sweet materials prepared by decomposing and saccharifying the starch of these raw materials with saccharifying enzymes. They are widely used in candy products, such as caramels, drops and jellies; Japanese-style confections, such as bean jams and sweet jellies of beans; and other foods, such as jams, syrups and foods boiled down in soy sauce.

Recently, with a growing attention to health in society, maltoligosaccharides, branched oligosaccharides, sugar alcohols, etc. have attracted attention from the viewpoints of growing *lactobacillus bifidus* in the testines, lowering sweetness and calorie, preventing tooth decay, and so forth. In order to obtain a starch syrup which significantly contains these saccarides, various investigations have been made into the kinds and combinations of enzymes to be added at

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the time of saccharification. However, these investigations have intended only to improve the saccharide components in starch syrups. Among the starch syrups made from the above-mentioned raw materials, no syrup is known to contain any effective component having value added. In other words, they have no characteristics in those components other than saccharides. Furthermore, with respect to raw material starch, nothing has been reported except for the above-mentioned materials which have been conventionally used.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide, using a novel raw material starch not reported so far, a powder form starch syrup which is excellent in nutritive balance with respect to various amino acids and minerals, and thus good for health.

The present inventors have made an intensive study toward the solution of the above assignment, and given attention to "*soba*" (buckwheat noodles) which is a Japanese traditional food. As a result, the inventors have found that a powder form buckwheat starch syrup prepared by liquefying starch from buckwheat flour contains various amino acids and minerals, as well as rutin contained in buckwheat flour which is effective in preventing arteriosclerosis. Thus, the buckwheat starch syrup is found to be very healthy in components and excellent in nutritive balance. The present invention has been achieved with these findings.

The present invention relates to a powder form

buckwheat starch syrup, namely, powdered buckwheat starch syrup, prepared by liquefying and spray-drying starch from buckwheat flour, as well as a method for preparing the same.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a chart showing the results of analysis of the powder form buckwheat starch syrup of the present invention by HPLC chromatography.

DETAILED DESCRIPTION OF THE INVENTION

Described below are preferred embodiments of a method for preparing the powder form buckwheat starch syrup of the present invention.

Generally, it is preferred that the raw material starch for a starch syrup contain as little protein as possible from the viewpoint of filtration and other treatment. Buckwheat flour is classified into surface layer flour, outside layer flour, inside layer flour, and whole layer flour containing the former three, according to the portion of buckwheat seeds ground into flour. In the present invention, not a whole layer flour having a high protein content but *"uchiko"* which is a flour mainly comprising medium layer flour is suitably used, since it has an extremely small protein content of about 3%. (*"Uchiko"* is a backwheat flour used in the preparation of backwheat noodles in order to prevent a dough from sticking on the board and the rolling pin.) In addition, roughly crushed buckwheat seeds (*"katsujitsu"*) may also be used.

First, 2 - 3 volumes of water is added to the raw material buckwheat flour (*"uchiko"*), which is then mixed and swollen to thereby obtain a starch milk (B x 25 - 30). This starch milk is filtered to remove foreign substances, etc. The pH of the filtrate is adjusted at 5.0 - 6.0, and then a liquefying enzyme is added thereto to liquefy the filtrate.

IFF000661164

As the liquefying enzyme to be used in this procedure, α - amylase is used. For example, Neospeedase manufactured by NAGASE BIOCHEMICALS, LTD. is suitably used.

For the liquefying, the liquefying enzyme is added in an amount of 0.1 - 1.0% by weight based on the solid content of the starch stock solution, and the resultant mixture is left at 88 - 90℃ for 1 - 2 hours.

At the completion of the liquefying, the starch sugar has a DE (dextrose equivalent) value of about 10 - 20.

In addition to the above-mentioned enzyme saccharification method, the liquefying of starch can also be performed by using an acid, such as oxalic acid.

After the completion of the liquefying reaction, the reaction solution is decolored with active carbon (granular carbon). Then, the solution is subjected to centrifugation or passed through a filter press to remove proteins as solid residue.

The above protein fraction recovered as solid residue is excellent in digestion, containing nutrient proteins, various amino acids, vitamins and minerals. Therefore, the protein fraction can be used as a food extender to be added to bean jams, dough for bread and cakes, etc. in contrast to the corresponding protein fraction from the conventional process using corn starch which has been used only as feed for chickens.

The solution so far treated is then dried with a spray dryer in which the temperature at the air-feeding state is set at 90 - 150 ℃. The moisture in the solution has been removed in an instant and the resultant product is air-dried. Then, the temperature at the open state is set at 80 - 90 ℃, and the product is recovered.

Thus, a desired buckwheat starch syrup in a powder form is obtained.

The thus obtained powder form buckwheat starch syrup of the present invention has a slight sweet taste and a fragrance, compared to conventional enzyme-saccharified starch syrups (the so-called "high-maltose starch syrup") having a strong sweet taste like sugar. When used in combination with concentrated products (condensed products, extracts, etc.) from milk, fruit, nuts, coffee, tea, or the like, the powder form buckwheat starch syrup of the present invention has an effect of reinforcing the tastes of these products.

The powder form buckwheat starch syrup thus obtained contains various oligosaccharides represented by maltose, maltotriose, maltotetraose and maltopentaose; various amino acids, such as arginine, alanine, glycine, glutamic acid and aspartic acid; minerals; vitamins and the like in good balance. Furthermore, it also contains rutin from buckwheat which is effective in improving the resistance of capillary vessels. Therefore, the powder form buckwheat starch syrup of the present invention is effective in preventing adult diseases, such as arteriosclerosis and hypertension, and yet it is excellent in nutritive balance. Thus, the syrup is very useful as a healthy food.

Utilizing the characteristic of bein powder, the buckwheat starch syrup of the present invention can be suitably used in various foods. For example, the powder form syrup may be used in ham and sausage as an extender, in creamy powder for coffee, in ice cream as a substitute for butterfat component, in various products from *sake* brewing, in fish flours (to be dusted over cooked rice),

in powder seasonings such as bouillon powder, in powder spices, in sauces for broiling and *teriyaki* and so on.

EFFECT OF THE INVENTION

According to the present invention, there is provided a buckwheat starch syrup in a powder form which contains various amino acids and minerals as well as rutin effective in preventing arteriosclerosis, and is thus healthy and excellent in nutritive balance. In addition, there is also provided a method for preparing the powder form buckwheat starch syrup.

PREFERRED EMBODIMENTS OF THE INVENTION

Now the present invention will be described in more detail with reference to Examples, which should not be construed to be limiting the scope of the present invention.

EXAMPLE 1

Preparation of Powder Form Buckwheat Starch Syrup

Two liters of water was added to 1 kg of raw material buckwheat flour (*"uchiko"*), which was then mixed and swollen to obtain a starch milk (B x 25 °). The pH of the starch milk was adjusted at 6.0, and 3 g of liquefying α-amylase (Neospeedase manufactured by NAGASE BIOCHEMICALS, LTD.) was added thereto. The resultant mixture was left at 90 ℃ for 2 hours for liquefying. At the completion of the liquefying, the starch sugar had a DE (dextrose equivalent) value of 20.

After the completion of the liquefication reaction, the reaction solution was decolored with active carbon (granular carbon), and then subjected to centrifugation or passed through a

filter press to remove proteins as solid residue. Next, the resultant solution was air-dried with a spray dryer (manufactured by Nicro) in which the temperature at the air-feeding state was set at 130 ℃. Then, the temperature at the open state was set at 80 ℃, and the resultant product was recovered. Thus, 200 g of a desired starch syryp in a powder form was obtained.

TESTING EXAMPLE 1

Characteristic and Component Analysis of

Powder Form Buckwheat Starch Syrup

The powder form buckwheat starch syrup obtained in Example 1 was analyzed on the following items.

(1) General component analysis and calory

Moisture content	2.6% (Heat-drying under reduced pressure)	
Proteins *1)	0.8%	(Kjeldahl method)
Lipids	0%	(Soxhlet extraction)
Fiber	0%	(Improved Henneberg-Stohmann method)
Ash	0.9%	(Direct ashing)
Sugars 2)	95.7%	
Energy *3)	386 kcal/100 g	
Iron	0.29 mg/100 g (*o*-phenanthroline absorptiometry)	
Calsium	109 mg/100 g (Potassium permanganate volumetric analysis)	
Potassium	128 mg/100 g (Atomic absorption spectrometry)	

*1) Nitrogen/Protein conversion factor: 6.25

*2) Calculation formula: 100 - (moisture content + proteins + lipids + fiber + ash)

*3) Energy conversion factors:

proteins; 4

lipids; 9

carbohydrates (fiber + sugars); 4

(2) Sugar composition

(Analytical conditions)

HPLC

Equipment used: Tosoh SC-8020 System (manufactured by Tosoh Corp.)

Column: Shodex SC-1011 (manufactured by Showa Denko K.K.) 8ϕ x 300 mm

Eluent: Distilled water

Temperature: 70℃

Detection: Differential refractive index detector RI-8020 (manufactured by Tosoh Corp.)

(Results)

Glucose	8.06%
Maltose	13.7%
Maltotriose	11.1%
Maltotetraose	7.72%
Maltopentaose	9.59%
Maltohexaose	13.4%

(3) Amino acid composition (Amino acid automatic analyzing method)

Arginine	5 mg/100 g

Lysine	1 mg/100 g
Histidine	1 mg/100 g
Phenylalanine	1 mg/100 g
Tyrosine	not detected
Leucine	not detected
Isoleucine	1 mg/100 g
Methionine	not detected
Valine	2 mg/100 g
Alanine	8 mg/100 g
Glycine	9 mg/100 g
Proline	not detected
Glutamic acid	11 mg/100 g
Serine	1 mg/100 g
Threonine	1 mg/100 g
Aspartic acid	4 mg/100 g

(4) Measurement of rutin content

(Method and analytical conditions)

(i) Preparation of test solution

1 g of test sample was accurately measured out and water was added thereto to give a 10 ml solution, which was used as a test solution.

(ii) HPLC chromatography

A 20 μ l standard solution of rutin (0.04 - 0.4 μ g rutin/ml water) was applied to HPLC chromatography and its working curve was prepared. Next, 20 μ l of the test solution was applied to HPLC chromatography and the rutin

concentration in the test solution was determined based on the working curve. Then, the rutin concentration in the test sample was calculated. The detection limit was set at 0.01 mg/100 g.

Equipment used: Model LC-10AS (manufactured by Shimadzu Seisakusho Ltd.)

Detector: UV Spectrophotometer SPD-10A (manufactured by Shimadzu Seisakusho Ltd.)

Column: YMC Pack ODS-A A-312

Mobile phase : 2.5 % Acetic acid-Mehtanol-Acetonitrile (35:5:10 V/V/V)

Wave length: 360 nm

Flow rate : 1 ml/min

(Results)

Rutin : 0.20 mg/100 g

The analysis results (chart) by HPLC chromatography are shown in Fig. 1.

REFERENCE EXAMPLE

Component Analysis of Buckwheat Flour *"Uchiko"*

Moisture content	14.0%	(Drying method)
Sugars	82.1%	(100 minus other components)
Ash	0.3%	(Drying method)
Crude protein	3.6%	(Kjeldahl method)
Degree of whiteness	72	(Atomic absorption spectrometry)

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A powdered buckwheat starch syrup prepared by liquefying starch from buckwheat flour and spray-drying the liquefied starch.

2. The powdered buckwheat starch syrup according to claim 1, wherein the buckwheat flour is "uchiko" or its equivalent which is a medium layer flour with a low protein content used in the preparation of buckwheat noodles in order to prevent a dough from sticking on the board and the rolling pin.

3. A method for preparing a powdered buckwheat starch syrup, which comprises liquefying starch from buckwheat flour and spray-drying the liquefied starch.

4. The method according to claim 3, wherein:

the buckwheat flour is "uchiko" or its equivalent which is a flour with a low protein content used in the preparation of buckwheat noodles in order to prevent a dough from sticking on the board and the rolling pin; and

for the liquefaction, a starch milk having a pH of 5.0 - 6.0 made from the buckwheat flour and water is heated in the presence of α-amylase or an acid.

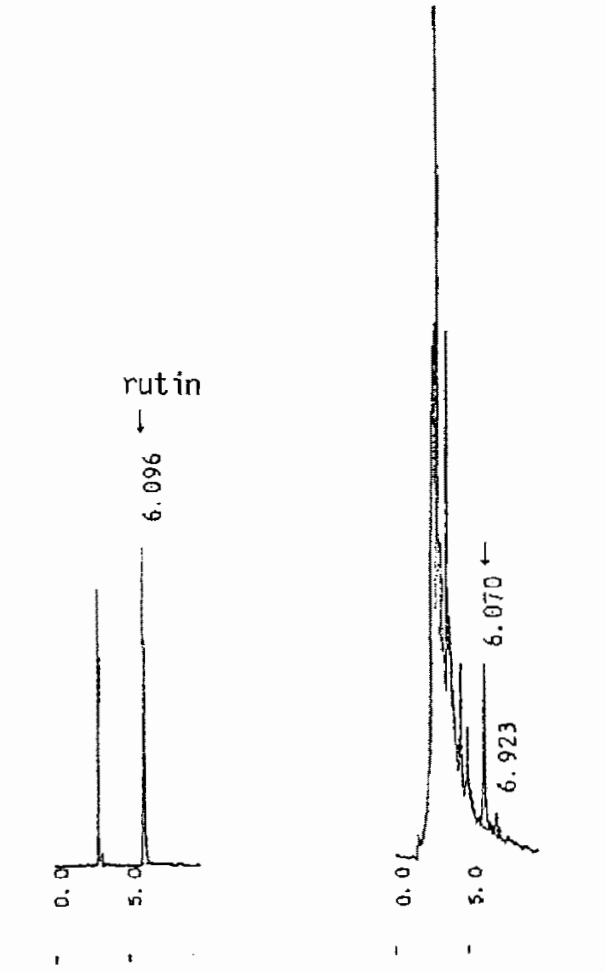
5. The method according to claim 4, wherein the starch milk is heated in the presence 0.1 to 1.0% by weight (based

on the solid content of the starch milk) of α-amylase at a temperature of 88 - 90°C, until a dextrose equivalent of from about 10 to about 20 is attained.

6. The method according to claim 4, wherein the starch milk is heated in the presence of an acid until a dextrose equivalent of from about 10 to about 20 is attained.

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FIG. 1



standard solution (8ng)

test solution

HPLC chromatography

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(3.10/3.09/3.3.3)

EP 0 461 197 B1

Description

BACKGROUND OF THE INVENTION

The present invention relates to methods for producing chewing gum. More particularly the invention relates to producing chewing gum containing Alitame.

Alitame is a high-potency sweetener with a chemical composition of L-α-Aspartyl-N-(2,2,4,4-tetramethyl-3-thietanyl)-D-alaninamide hydrate. This sweetener, which is not yet approved for use in food products and chewing gum, is being considered by the FDA as a food additive. The manufacturer of Alitame is the Pfizer Corporation of Groton, Connecticut. This highly consumer-acceptable, high-potency sweetener gives chewing gum a fast, strong release that is not desirable.

Alitame has been used in chewing gum. Such use has been disclosed in several patents. U.S. Patent No. 4,411,925 discloses simple addition of Alitame in gum. U.S. Patent No. 4,536,396 discloses combinations of Alitame and Acesulfame K in foods including chewing gum.

Alitame has been found to be relatively unstable and susceptible to degradation in chewing gums containing certain ingredients. This result was rather unexpected since Alitame has been shown to be much more stable in aqueous solutions than aspartame, another dipeptide high-potency sweetener, and therefore, was expected to he much more stable in chewing gums.

Further, at the concentrations usually used in chewing gums, Alitame has a pure and rapidly perceptible sweet taste that does not linger. However, when Alitame is added to chewing gum at a level of about 0.01%-0.04%, the sweetener gives the chewing gum a fast, intense sweetness which dissipates rather quickly, leaving a strong flavor that is less than pleasant. It would be considered a significant improvement to a chewing gum to have Alitame protected against degradation, or to have its sweetness released as the flavor in the gum is released, thus balancing the overall taste perception. Thus, methods of treating the high-potency sweetener to protect against degradation and to delay the release of sweetness in balance with the chewing gum flavor would therefore be a definite improvement.

Efforts have been directed at perfecting the use of other high-potency sweeteners within the chewing gum formulation, to thereby increase the shelf-life stability of the ingredients, i.e. the protection against degradation of the high-potency sweetener over time.

EP Patent 0302024 teaches providing a chewing gum with at least 2 layers, one of which includes aspartame, the other of which includes gum base and flavouring agents. The layers are provided on the opposite sides of a protective film that is disposed between the 2 layers, so that the aspartame is separated from the flavouring agents in the second layer and does not contact them.

U.S. Patent No. 4,139,639 to Bahoshy et al. teaches a process of "fixing" aspartame by co-drying (by spray drying or fluid-bed coating) a solution containing aspartame and an encapsulating agent, such as gum arabic, to thereby surround and protect the aspartame in the gum during storage.

U.S. Patent No. 4,384,004 to Cea et al. teaches a method of encapsulating aspartame with various solutions of encapsulating agents using various encapsulation techniques, such as spray drying, in order to increase the shelf-stability of the aspartame.

Efforts have also been devoted to controlling release characteristics of various ingredients in chewing gum. Most notably, attempts have been made to delay the release of sweeteners and flavors in various chewing gum formulations to thereby lengthen the satisfactory chewing time of the gum. Delaying the release of sweeteners and flavors can also avoid undesirable overpowering burst of sweetness or flavor during the initial chewing period. On the other hand, some ingredients have been treated so as to increase their rate of release in chewing gum.

Some patents disclose how a sweetener like aspartame can be physically modified to control the release rate in chewing gum. For example, U.S. Patent No. 4,597,970 to Sharma et al. teaches a process for producing an agglomerated sweetener wherein the sweetener is dispersed in a hydrophobic matrix consisting essentially of lecithin, a glyceride, and a fatty acid or wax having a melting point between 25 °C and 100 °C. The method disclosed uses a spray-congealing step to form the sweetener-containing matrix into droplets, followed by a fluid-bed second coating on the agglomerated particles.

U.S. Patent Nos. 4,515,769 and 4,386,106, both to Merrit et al., teach a two step process for preparing a delayed release flavorant for chewing gum. In this process, the flavorant is prepared in an emulsion with a hydrophilic matrix. The emulsion is dried and ground and the particles are then coated with a water-impermeable substance.

U.S. Patent No. 4,230,687 to Sair et al. teaches a process for encasing an active ingredient to achieve gradual release of the ingredient in a product such as chewing gum. The method described involves adding the ingredient to an encapsulating material in the form of a viscous paste. High-shear mixing is used to

achieve a homogeneous dispersion of the ingredient within the matrix, which is subsequently dried and ground.

WO 89/05589 to Zibell teaches coating a quantity of previously coated high potency sweetener particles, particularly aspartame, with zein in order to produce a chewing gum with delayed release.

U.S. Patent No. 4,634,593 to Stroz et al. teaches a method for producing controlled release sweeteners for confections, such as chewing gum. The method taught therein involves the use of an insoluble fat material which is mix mulled with the sweetener.

In light of the problem that Alitame degrades in the presence of some chewing gum ingredients, there presently exists a need to prevent this degradation. There also exists the need to control Alitame's release from the chewing gum so as to increase overall taste perception. None of the prior art indicated specifically addresses either a means to delay the degradation of Alitame in chewing gum or a means to slowly release the sweetener. Thus a means to both delay the degradation and control the release of Alitame would be highly desired.

The present invention includes a method of making chewing gum with Alitame and the chewing gum itself. The chewing gum of the present invention comprises in intimate admixture, a gum base from 5 to 95% of the chewing gum composition, a bulking agent from 10 to 90% of the chewing gum composition, a flavouring agent from 0.1 to 10% of the chewing gum composition, coated Alitame wherein at least one of the said gum base ingredients, bulking agents, or flavouring agents is also an Alitame degradation agent and wherein the Alitame is sufficiently coated to slow Alitame degradation due to the degradation agent so that at least 60% of an original amount of Alitame in the chewing gum remains after 8 weeks of storage at 29 °C (85 °F), excepting that the coated Alitame is not blended with Acesulfame K prior to coating and the coated Alitame is not coated with zein.

In accordance with a preferred embodiment of this invention the Alitame is coated by a material in order to slow Alitame degradation The material coating the Alitame is selected from the group consisting of acrylic polymers, acrylic copolymers, carboxyvinyl polymers, polyamides, polystyrene, polyvinyl acetate, polyvinyl acetate phtalate and, Polyvinylpyrrolidone.

In accordance with another preferred embodiment of this invention, the Alitame is coated with natural gums like agar, alginates, guargum, gum tragacanth, xanthan gum, or carrageenan.

In accordance with still another preferred embodiment of this invention, the Alitame is coated with a cellulose derivative selected from the group consisting of ethyl cellulose, methyl cellulose, sodium hydroxymethyl cellulose, hydroxypropylmethyl cellulose; or dextrin; gelatin or modified starches.

In another preferred embodiment, the Alitame used to sweeten the chewing gum is coated by shellac or Zein.

An advantage of this invention is that Alitame's unstability in chewing gum can be controlled by separating the sweetener from the substances capable of degrading it.

Furthermore, the Alitame may be slowly released in the gum, resulting in a chewing gum which is sweeter and more gratifying to the consumer.

Another advantage rendered by this invention is that a higher quantity of the sweetener Alitame can be used without the consumer realizing a sudden burst of sweetness. The end product has a gradual and delayed release of sweetness which is compatible with the flavor release in most chewing gums.

The present invention together with the attendant objects and advantages will be best understood with reference to the detailed description below.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The chewing gum of the present invention includes a gum base, a bulking agent, a flavoring agent, the sweetener, Alitame and a means to separate the Alitame from substances in the gum capable of degrading the Alitame.

In sugarless gums, a high-potency sweetener is usually used with a sugar alcohol. The sugar alcohol provides some sweetness, but is predominantly used as a bulking agent. Suitable sugar alcohols for sugarless gums include sorbitol, mannitol, xylitol, hydrogenated starch hydrolysates, maltitol, and the like, as well as combinations thereof. Early tests with sugarless gums containing Alitame showed unexpected Alitame degradation. It was theorized that the sugar alcohols used in the gum had an adverse effect upon Alitame. The results in Tests 1-5 discussed below confirmed this theory. It is also thought that some flavor ingredients, other aliditols or some base ingredients may cause Alitame degradation.

As stated previously, Alitame releases very quickly from chewing gum during the early stages of mastication of the gum because of its high solubility in water. Physical modifications of the sweetener by encapsulation with another substrate may not only slow its release in chewing gum by reducing the

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dissolution rate of Alitame, but may also reduce or eliminate the degradation of Alitame. Any standard technique which gives partial or full encapsulation of the Alitame sweetener can be used. These techniques include, but are not limited to, agglomeration, spray drying, fluid-bed coating and coacervation with the most preferred embodiments described below in Examples 8, 9 and 12. These encapsulation techniques that give partial encapsulation or full encapsulation can be used individually or in any combination in a single step process or multiple step process. Generally, improved stability of sweetener is obtained in multistep processes like spray drying the sweetener and then fluid-bed coating or agglomeration of the resultant powder.

The encapsulation techniques here described are standard coating techniques and generally give varying degrees of coating from partial to full coating, depending on the coating compositions used in the process. Also, the coating compositions may be susceptible to water permeation to various degrees. Generally, compositions that have, good film-forming properties and low water solubility give better stability of the sweetener. Such compositions include acrylic polymers and copolymers, carboxyvinyl polymer, polyamides, polystyrene, polyvinyl acetate, polyvinyl acetate phthalate, and polyvinyl-pyrrolidone Two standard food-grade coating materials that are good film formers but which are not water soluble are shellac and Zein. Others which are more water soluble, and good film formers, are materials like natural gums like agar, alginates, guar gum, gum tragacanth, xanthangum, or carrageenan, a wide range of cellulose derivatives like ethyl cellulose, methyl cellulose, sodium hydroxymethyl cellulose; and hydroxypropylmethyl cellulose, dextrin, gelatin, and modified starches. These ingredients, which are generally approved for food use, also give an improved stability when used as an encapsulant for Alitame. Other encapsulants like acacia or maltodextrin can also encapsulate Alitame, but give very little improvement in the stability of Alitame in gum.

The amount of coating or encapsulating material on the sweetener Alitame also controls the stability improvement of Alitame in chewing gum. Generally, the higher the level of coating and the lower the amount of degradation of Alitame. To obtain the desired stability improvement, the encapsulant should be set at a minimum of about 10% of the coated sweetener. Preferably, the encapsulant should be at least about 15% of the coated sweetener, and most preferably should be a minimum of about 20% of the coated sweetener.

Another method of improving the stability of Alitame is to agglomerate or granulate the sweetener with an agglomerating agent which partially coats the sweetener. This method includes the step of mixing the sweetener and agglomerating agent with a small amount of water or solvent. The mixture is prepared in such a way as to have individual wet particles in contact with each other so that a partial coating can be applied. After the water or solvent is removed, the mixture is ground and used as a powdered, coated sweetener.

Materials that can be used as the agglomerating agent are the same as those used in encapsulation mentioned previously. However, since the coating is only a partial encapsulation and the Alitame sweetener is very water soluble, some agglomerating agents are more effective in improving Alitame stability than others. Some of the better agglomerating agents are the organic polymers like acrylic polymers and copolymers, polyvinyl acetate, polyvinylpyrrolidone, shellac and Zein. Other agglomerating agents are not as effective in giving the sweetener a delayed release as are the above-mentioned polymers but can be used to give improved stability. These other agglomerating agents include, but are not limited to, natural gums like agar, alginates, guar gums, gum tragacanth, xanthan gum, or carrageenan; a wide range of cellulose derivatives like ethyl cellulose, methyl cellulose, sodium hydroxymethyl cellulose, hydroxypropylmethyl cellulose; dextrin, and modified starches; and gelatin. Even though the agglomerated sweetener is only partially coated, when the quantity of coating is increased compared to the quantity of Alitame sweetener, the stability of Alitame can be improved to a greater degree. The level of coating used in the agglomerated product is a minimum of about 5%. Preferably the coating level is a minimum of about 15% and more preferably about 20%.

The Alitame sweetener may be coated in a two-step process or multiple step process. The sweetener may be encapsulated with any of the materials as described previously and then the encapsulated sweetener can be agglomerated as described previously to obtain an encapsulated/agglomerated/sweetenerproduct that could be used in chewing gum to give an improved Alitame stability.

In another embodiment of this invention, Alitame sweetener may be absorbed onto another component which is porous, thus becoming entrapped in the matrix of the porous component. Common materials used for absorbing the sweetener include, but are not limited to, silicas, silicates, pharmasorb clay, spongelike beads or microbeads, amorphous sugars like dried dextrose, sucrose, amorphous carbonates and hydroxides, including aluminum and calcium lakes, vegetable gums and other spray dried materials.

Depending on the type of absorbent material and how it is prepared, the amount of Alitame sweetener that can be loaded into the absorbent will vary. Generally, material like polymers or spongelike beads or microbeads, amorphous sugars and amorphous carbonates and hydroxides absorb about 10% to about 40% of the weight of the absorbent. Other materials like silicas and pharmasorb clays may be able to absorb about 20% to about 80% of the weight of the absorbent.

The general procedure for absorbing the sweetener onto the absorbent is as follows. An absorbent like fumed silica powder can be mixed in a powder blender and an aqueous solution of the Alitame sweetener can be sprayed onto the powder as mixing continues. The aqueous solution can be about 5% to 30% Alitame solids, and higher solid levels may be used if temperatures up to 90 °C are used. Generally, water is the solvent, but other solvents like alcohol could also be used if approved for use in food. As the powder mixes, the liquid is sprayed onto the powder. Spraying is stopped before the mix becomes damp. The still flowing powder is removed from the mixer and dried to remove the water or other solvent, and ground to a specific particle size.

After the Alitame sweetener is absorbed onto an absorbent or fixed onto an absorbent, the fixative/sweetener should be coated by encapsulation or agglomeration. Either full or partial coating procedures may be used in the process. Full encapsulation may be obtained by coating with a polymer as fluid-bed coating, fiber spinning, coacervation, or any other standard techniques. A partial encapsulation or coating can be obtained by agglomeration of the fixative/sweetener mixture using any of the materials discussed above.

The three methods of use to obtain an improved stability of Alitame sweetener are: (1) encapsulation by spray drying, fluid-bed coating, fiber spinning or coacervation to give full or partial encapsulation, (2) agglomeration to give partial encapsulation and (3) fixation or entrapment/absorption plus encapsulation or agglomeration which also gives partial encapsulation. These three methods, combined in any usable manner which physically isolates the Alitame sweetener to improve its stability, are included in this invention.

Other methods of treating the Alitame sweetener to physically isolate the sweetener from other chewing gum ingredients may also have some effect on its release rate and stability. The Alitame sweetener may be added to the liquid inside a liquid center gum product. The center fill of a gum product may comprise one or more carbohydrate syrups, thickeners, flavors, acidulants, colors, and sugars in conventional amounts. The ingredients are combined in a conventional manner. The Alitame sweetener is dissolved in the center-fill liquid and the amount of Altimate sweetener added to the center-fill liquid is about 5 ppm to about 400 ppm by weight of the entire chewing gum formula. This method of using Alitame sweetener in chewing gum can allow for a lower usage level of the sweetener, can give the sweetener a smooth release rate, and can reduce or eliminate any possible reaction of the sweetener with gum base, flavor components or alditols, yielding improved shelf stability.

Another method of isolating Alitame sweetener is to use it in the coating/panning of a pellet chewing gum. Pellet or ball gum is prepared as conventional chewing gum, but formed into pellets that are pillow shaped or into balls. The pellets/balls can then be sugar coated or panned by conventional panning techniques to make a unique sugar coated pellet gum. Alitame sweetener is very stable and highly water soluble, and can be easily added to a sugar solution prepared for sugar panning. Alitame can also be added as a powder blended with other powders often used in some types of conventional panning procedures. Using Alitame sweetener isolates the sweetener from other gum ingredients and modifies its stability in chewing gum. Levels of use of Alitame may be about 10 ppm to about 500 ppm in the coating and about 5 ppm to about 200 ppm of the weight of the chewing gum product. The weight of the coating may be about 20% to about 50% of the weight of the finished gum product.

Conventional panning procedures generally coat with sucrose, but recent advances in panning have allowed the use of other carbohydrate materials to be used in the place of sucrose. Some of these components include, but are not limited to, dextrose, maltose, and palatinose, and other new carboydrates or a combination thereof. These materials may be blended with panning modifiers including, but not limited to, gum arabic, maltodextrins, corn syrup, gelatin, cellulose type materials like carboxymethyl cellulose, or hydroxymethyl cellulose, starch and modified starches, natural gums like alginates, locust bean gum, xanthan gum, and gum tragacanth, insoluble carbonates like calcium carbonate or magnesium carbonate and talc. Antitack agents may also be added as panning modifiers which allow the use of a variety of carbohydrates to be used in the development of new panned or coated gum products. Flavors may also be added with the sugar coating and with the Alitame sweetener to yield unique product characteristics.

Another type of pan coating would also isolate the Alitame sweetener from the chewing gum ingredients. This technique is referred to as film coating and is more common in pharmaceuticals than in chewing gum, but procedures are similar. A film like shellac, Zein, or cellulose-type material is applied onto

a pellet-type product forming a thin film on the surface of the product. The film is applied by mixing the polymer, a plasticizer and a solvent (pigments are optional) and spraying the mixture onto the pellet surface. This is done in conventional type panning equipment, or in more advanced side-vended coating pans. When a solvent like alcohol is used, extra precautions are needed to prevent fires and explosions, and specialized equipment must be used. Since Alitame is highly soluble in alcohol, solvent films can be added that contain the Alitame sweetener. This will give a unique sweetness release to a film coated product.

Some film polymers can use water as the solvent in film coating. Recent advances in polymer research and in film coating technology eliminates the problem associated with the use of solvents in coating. These advances make it possible to apply aqueous films to a pellet or chewing gum product. As Alitame sweetener is highly water soluble, it can be added to this aqueous film solution and applied with the film to the pellet or chewing gum product. The aqueous film or even the alcohol solvent film may also contain a flavor along with the polymer and plasticizer. By adding Alitame sweetener to the polymer/plasticizer/solvent system either as an emulsion or solution, the sweetener can add sweetness to the flavor and a balanced flavor/sweetness can be obtained. The Alitame sweetener can also be dissolved in the aqueous solvent and coated on the surface with the aqueous film. This will give a unique sweetness release to a film coated product.

The previously described coated sweetener may readily be incorporated into a chewing gum composition. The remainder of the chewing gum ingredients are non-critical to the present invention. That is, the coated particles of high-potency sweetener can be incorporated into conventional chewing gum formulations in a conventional manner. Naturally, the preferred chewing gum formulation is a sugarless chewing gum. However, the coated particles of high potency sweetener may also be used in sugar chewing gum to reduce or eliminate the degradation of Alitame due to the flavor in the gum. The coated high-potency sweetener may be used in either regular chewing gum or bubble gum.

In general, a chewing gum composition typically comprises a water soluble bulk portion, a water-insoluble chewable gum base portion and typically water-insoluble flavoring agents. Additionally, the water soluble portion dissipates with a portion of the flavoring agent over a period of time during chewing, while the gum base is retained in the mouth throughout the chew.

The insoluble gum base generally comprises elastomers, resins, fats and oils, waxes, softeners and inorganic fillers. Elastomers may include polyisobutylene, isobutylene-isoprene copolymer and styrene butadiene rubber as well as natural latexes such as chicle. Resins include polyvinylacetate and terpene resins. Fats and oils may also be included in the gum base, including tallow, hydrogenated and partially hydrogenated vegetable oils, and cocoa butter. Commonly employed waxes include paraffin, microcrystalline and natural waxes such as beeswax and carnauba. According to the preferred embodiment of the present invention, the insoluble gum base constitutes between about 5 to about 95 percent by weight of the gum. More preferably, the insoluble gum base comprises between 10 and 50 percent by weight of the gum and most preferably about 20 to about 35 percent by weight of the gum.

The gum base typically includes a filler component. The filler component may be calcium carbonate, magnesium carbonate, talc, dicalcium phosphate or the like. The filler may constitute between about 5 and about 60 percent by weight of the gum base. Preferably, the filler comprises about 5 to about 50 percent by weight of the gum base.

Gum bases typically also contain softeners, including glycerol monostearate and glycerol triacetate. Further, gum bases may also contain optional ingredients such as antioxidants, colors, and emulsifiers. The present invention contemplates using any commercially acceptable base.

The water soluble portion of the chewing gum comprises softeners, sweeteners, flavoring agents and combinations thereof. Softeners are added to the chewing gum in order to optimize the chewability and mouth feel of the gum. Softeners, also known in the art as plasticizers or plasticizing agents, generally constitute between about 0.5 to about 15.0 percent by weight of the chewing gum. Softeners contemplated by the invention include glycerin, lecithin, and combinations thereof. Further, aqueous sweetener solutions such as those containing sorbitol, hydrogenated starch hydrolysates, corn syrup and combinations thereof may be used as softeners and binding agents in gum.

A flavoring agent may be present in the chewing gum in an amount within the range of from about 0.1 to about 10.0 weight percent of the gum. The flavoring agents may comprise essential oils, synthetic flavors, or mixtures thereof including, but not limited to, oils derived from plants and fruits such as citrus oils, fruit essences, peppermint oil, spearmint oil, clove oil, oil of wintergreen, anise and the like. Artificial flavoring components are also contemplated for use in gums of the present invention. Those skilled in the art will recognize that natural and artificial flavoring agents may be combined in any sensorally acceptable blend. All such flavors and flavor blends are contemplated by the present invention.

Optional ingredients such as colors, emulsifiers, and pharmaceutical agents may be added to the chewing gum. In general, chewing gum is manufactured sequentially adding the various chewing gum ingredients to a commercially available mixer known in the art. After the ingredients have been thoroughly mixed, the gum mass is discharged from the mixer and shaped into the desired form such as by rolling into sheets and cutting into sticks, extruding into chunks or casting into pellets.

Generally, the ingredients are mixed by first melting the gum base and adding it to the running mixer itself. Color or emulsifiers may also be added at this time, along with syrup and a portion of the bulking agent. Further portions of the bulking agent may then be added to the mixer. A flavoring agent is typically added with the final portion of the bulking agent. A coated Alitame sweetener is added when convenient.

The entire mixing procedure typically takes from five to fifteen minutes, but longer mixing times may sometimes be required. Those skilled in the art will recognize that many variations of the above described procedure may be followed.

Tests 1-5

Tests 1-4 and comparative Test 5 were carried out to see the effect of alditols (sugar alcohols and glycerol) found in sugarless gum upon Alitame. A 0.01% Alitame aqueous solution was divided equally into 5 portions. In Tests 1-3, different sugar alcohols were added to each of the first three portions in proportions of 5 parts sugar alcohol and 95 parts Alitame solution. In test 4, a 75/25 blend of Lycasin/glycerol was added to the fourth portion in proportion of 5 parts alditol and 95 parts Alitame solution. In comparative Test 5, there was no addition of sugar alcohol. Next, each test was divided in half and each half adjusted to either a pH of 5 or 7. Each test was further divided in half again and one half was stored at room temperature while the second half was stored at 120°F. The Alitame stability results are indicated in the table below.

Percent Original Alitame Remaining After 12 Weeks					
		24°C(75°F) pH 5	24°C(75°F) pH 7	49°C(120°F) pH 5	49°C(120°F) pH 7
Test 1	5% Glycerol	100	64	69	0
Test 2	5% Sorbitol	100	100	75	0
Test 3	5% Mannitol	100	94	80	0
Test 4	5% Lycasin/Glycerol blend	100	94	77	47
Test 5	-	97	100	95	79

Analysis of the results showed that, unexpectedly, Alitame degraded at a much quicker rate in solutions of sugar alcohols and glycerol than solutions not containing any alditols, and that glycerol and low molecular weight sugar alcohols seemed to particularly cause Alitame degredation.

Examples 1-16

Comparative Example 1 and Examples 2-16 were performed to see the effect of coating Alitame and then adding the resultant product to a chewing gum formulation. Various coatings and modes of application of coating material were performed in Examples 2 through 16. All of the examples used the following formulae based on the total weight of the gum.

	%
Base	25.5
Lecithin	0.2
Sorbitol	49.4
Mannitol	8.0
Lycasin	6.8
Glycerol	8.6
Peppermint Flavor	1.46
Active Alitame	0.04

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All of the examples were generally prepared by providing the individual ingredients, combining them, and preparing them into pieces for testing. The gum base was melted and added to a running mixer. Then the lecithin and sorbitol were added in the first three minutes of mixing. The mannitol, lycasin, glycerol, and coated Alitame were added within the next two to three minutes. The flavor was added last at minute eight. The entire mixing procedure lasted thirteen minutes. The composition was then discharged from the mixer and formed into pellets. The following encapsulated Alitame samples were prepared and used in the above gum formulation:

Example 1 - Alitame powder was added directly to the gum.

Example 2 - A 10% aqueous solution of Alitame was sprayed onto a precipitated silica to absorb the sweetener. The mixture was dried and screened through 600µm (30-mesh)sieve to remove lumps. The final product was 18% Alitame, 80.4% silica gel, and 1.6% moisture.

Example 3 - A 93% stearic acid mixture was prepared by melting stearic acid and blending it with 7% of the product of Example 2. This mixture was spray chilled to yield a product containing 1.3% Alitame, 5.7% silica gel, and 93% stearic acid.

Example 4 - A 20% stearic acid/80% Alitame powder mixture was obtained by agglomerating Alitame and molten stearic acid, and cooling and grinding the resulting product.

Example 5 - A 20% paraffin wax (M.P. = 57 °C(135 °F))/80% Alitame powder mixture was obtained by agglomerating Alitame and molten wax, and cooling and grinding the resulting product.

Example 6 - A 20% microcrystalline wax (M.P. = 82 °C(180 °F))/80% Alitame powder mixture was obtained by agglomerating Alitame and molten wax, and cooling and grinding the resulting product.

Example 7 - A 97% stearic acid/3% Alitame mixture was spray chilled together to give a final product containing 3% Alitame.

Example 8 - A 15% HPMC/85% active Alitame powder mixture was obtained by agglomerating an HPMC and Alitame mixture blended together, with water being added, and the resulting product was dried and ground. A final product containing 81% Alitame, 15% HPMC, and 4% moisture was obtained.

Example 9 - Alitame was agglomerated with HPMC in a ratio of 85/15 sweetener/HPMC. After drying and grinding, the resulting powder was agglomerated with a 15% solids, high pH, aqueous solution of Zein. After drying and grinding a final product containing 77% Alitame, 14% HPMC, 6% Zein, and 3% moisture was obtained.

Example 10 - Alitame was film dried with gelatin by dissolving 300 Bloom gelatin in a 10% aqueous solution of Alitame at a ratio of 30/70 gelatin/Alitame. The mixture was spread to a thin film on trays and dried at 43 °C(110 °F) The resulting product was ground and contained 18% Alitame, 75% gelatin, and 7% moisture.

Example 11 - Alitame was film dried with gelatin as in Example 10. After grinding, the resulting powder was agglomerated with a 15% solids, high pH, aqueous solution of Zein. After drying and grinding, a final product containing 16% Alitame, 68% gelatin, 8% Zein, and 8% moisture was obtained.

Example 12 - Powdered Alitame and powdered PVAc were blended together in a ratio of 10/90 Alitame/PVAc. The blend was added to a fiber spinning extruder wherein the softened PVAc entrapped the sweetener. This method is fully described in pending U.S. Patent Application Serial No. 07/340,384, incorporated herein by reference.

Example 13 - A 30% solution of 10 parts maltodextrin and 1 part Alitame was spray dried resulting in a product that had 8% active Alitame.

Example 14 - A blend of 100/1 mannitol/Alitame was agglomerated together with water, dried and ground.

Example 15 - A 30% solids solution of alcoholic shellac was used to fluid bed coat the product of Example 14. The final product was about 20% shellac, 79.2% mannitol, and had an active Alitame level at 0.8%.

Example 16 - A 20% solids solution of alcoholic Zein was used to fluid bed coat the product of Example 14. The resulting sample was screened into various particle sizes. Selected samples were analyzed for active Alitame and used in the above gum formulation.

Three such samples were:

a) Remaining on a 425µm (40-mesh)- active Alitame 0.73%

b) through 425µm (40-mesh), remaining on a 250µm (60-mesh)-active Alitame was 0.81%

c) through 150µm (200-mesh), remaining on a 75µm (200-mesh)-active Alitame was 0.95%.

After the coated Alitame of Examples 1-16 were added to the gum formulation, each gum formulation was formed into pellets and placed in six sealed pouches and stored at 29 °C (85 °F). Immediately a pouch was removed and analyzed for the percentage of Alitame. Thereafter, a pouch was analyzed for the percentage of Alitame remaining at the end of each of the following weeks: 1, 2, 4, 6 and 8 weeks. Results

after 8 weeks of storage are given in Table II and calculated as percentage of Alitame remaining in the gum based on the week 0 analysis. The results have been listed generally in rank of effectiveness in preventing Alitame degradation.

TABLE II

Example	Encapsulant	Coating	Percent Alitame Remaining After 8 Weeks at (85°F) 29°C
12	Fiber Spun with PVAc	90% PVAc	100
8	Agglomeration with HPMC	15% HPMC	100
9	Agglomeration with HPMC and agglomeration with Zein	14% HPMC 6% Zein	92
16a	Agglomeration with Mannitol and fluid bed coated with Zein (remaining on 40 mesh)	70% Mannitol 27% Zein	100

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TABLE II CONT'D

Example	Encapsulant	Coating	Percent Alitame Remaining After 8 Weeks at (85°F) 29°C
16b	Agglomeration with Mannitol and fluid bed coated with Zein through 40-mesh, remaining on 60-mesh)	82% Mannitol 17% Zein	92
16c	Agglomeration with Mannitol and fluid bed coated with Zein, (through 100-mesh, remaining on 200-mesh	4% Zein	95% Mannitol 47
10	Film dried with with Gelatin	75% Gelatin	81
11	Film dried with Gelatin and agglomeration with Zein	68% Gelatin 8% Zein	88
4	Agglomeration with Stearic Acid	20% Stearic Acid	48
6	Agglomeration with micro-crystalline Wax	20% wax	42
5	Agglomeration with Paraffin Wax	20% wax	34
7	Spray Chilled with Stearic Acid	97% stearic Acid	16
2	Absorption on Silica Gel	80.4% silica Gel	33
3	Absorption on Silica Gel and spray chill with stearic acid	5.7% silica Gel 93% stearic acid	28
15	Agglomeration with Mannitol and fluid bed coated with Shellac	65% Mannitol 34% Shellac	33
14	Agglomeration with Mannitol	94% Mannitol	34
13	Spray dried with maltodextrin	92% malto-dextrin	25
1	None (Control)	None	32

Results in Table II show that the good film formers like HPMC, gelatin, Zein, and PVAc give good protection to yield significantly improved Alitame stability compared to a control. As can be seen from the results, materials like maltodextrin used in spray drying, mannitol used in agglomeration and silica gel used for absorption of the Alitame offer very little protection.

As demonstrated in Examples 16a, 16b and 16c, a minimum amount of Zein coating is required to give adequate protection for Alitame. This level is about 15%. A similar coating level would be expected for shellac and gelatin. In example 15, evidently insufficient Shellac was coated onto the Alitame/Mannitol sample blends (Example 14) to provide significant protection of the Alitame.

The use of waxes or stearic acid do not show a significant improvement in Alitame stability in either agglomerating or spray chilling. It is speculated that the waxes and stearic acid may have a negative effect on the stability of Alitame.

Claims

1. A chewing gum composition comprising, in intimate admixture,
   a) 5 to 95% of a gum base;
   b) 10 to 90% of a bulking agent;
   c) 0.1 to 10% of a flavouring agent; and
   d) coated Alitame wherein at least one of the said gum base ingredients, bulking agents, or flavouring agents is also an Alitame degradation agent and wherein the Alitame is sufficiently coated to slow Alitame degradation due to the degradation agent so that at least 60% of an original amount of Alitame in the chewing gum remains after 8 weeks of storage at 29 °C (85 °F), excepting that the coated Alitame is not blended with Acesulfame K prior to coating and the coated Alitame is not coated with zein.

2. The chewing gum composition of claim 1 wherein the Alitame comprises from 0.005 to 0.10% of the total gum composition.

3. The chewing gum composition of claim 1 or claim 2 wherein the chewing gum is a sugarless chewing gum.

4. The chewing gum composition of any one of claims 1 to 3 wherein the bulking agent comprises a sugar alcohol selected from sorbitol, mannitol, xylitol, malitol, hydrogenated starch hydrolysates and mixtures thereof.

5. The chewing gum of any one of claims 1 to 4 wherein the Alitame is coated by a material selected from acrylic polymers, carboxyvinyl polymers, polyamides, polystyrene, polyvinyl acetate, polyvinyl acetate phtalate, polyvinylpyrolidone and copolymers thereof.

6. The chewing gum composition of any one of claims 1 to 4 wherein the Alitame is coated by a material selected from agar alginates, guar gum, gum tragacanth, carrageenan, and xanthan gum.

7. The chewing gum composition of any one of claims 1 to 4 wherein the Alitame is coated by a material which comprises a cellulose derivative selected from ethyl cellulose, methyl cellulose, sodium hydroxymethyl cellulose, hydroxypropylmethyl cellulose and modified starches.

8. The chewing gum composition of any one of claims 1 to 4 wherein the Alitame is coated by a material selected from of shellac, and gelatin.

9. A method of making a chewing gum with Alitame comprising the steps of:
   a) providing from 5 to 95% gum base, 10 to 90% of a bulking agent, and 0.1 to 10% of a flavoring agent, at least one of said bulking and flavoring agents also being an Alitame degradation agent;
   b) coating a quantity of Alitame with a coating material which slows Alitame degradation due to the Alitame degradation agent so that at least 60% of an original quantity of Alitame formulated in the gum remains after 8 weeks of storage at 29 °C (85 °F), excepting that the coated Alitame is not blended with Acesulfame K prior to coating and the coated Alitame is not coated with zein, and
   c) intimately mixing the coated Alitame, the gum base, bulking agent and flavoring agent to make a chewing gum composition.

10. The method of claim 9 wherein the quantity of Alitame added to the other ingredients is between 0.005 to 0.10% of the total gum composition.

11. The method of claim 9 or claim 10 wherein the chewing gum is a sugarless chewing gum.

12. The method of any one of claims 9 to 11 wherein the bulking agent further comprises a sugar alcohol selected from sorbitol, mannitol, xylitol, maltitol, hydrogenated starch hydrolysates and mixtures thereof.

13. The method of any one of claims 9 to 12 wherein the coating material is selected from acrylic polymers, carboxyvinyl polymers, polyamides, polystyrene, polyvinyl acetate, polyvinyl acetate phtalate, polyvinylpyrolidone and copolymers thereof.

14. The method of any one of claims 9 to 12 wherein the coating material is selected from agar alginates, guar gum, gum tragacanth, carrageenan, and xanthan gum.

15. The method of any one of claims 9 to 12 wherein the coating material comprises a cellulose derivative selected from ethyl cellulose, methyl cellulose, sodium hydroxymethyl cellulose, hydroxypropylmethyl cellulose and modified starches.

16. The method of any one of claims 9 to 12 wherein the coating material is selected from shellac, and gelatin.

17. The method of any one of claims 9 to 16 wherein the step of coating the Alitame comprises:
a) mixing a quantity of Alitame with an encapsulating material; and
b) agglomerating the encapsulated Alitame.

18. The method of any one of claims 9 to 16 wherein the step of coating the Alitame comprises:
a) mixing a quantity of Alitame with a spray drying solvent and an encapsulating material; and
b) spray drying the mixture in such a way as to encapsulate the Alitame.

19. The method of any one of claims 9 to 16 wherein the step of coating the Alitame comprises fluid bed coating a quantity of Alitame with an encapsulating material dissolved or dispersed in a solvent.

20. A method of making a chewing gum with Alitame comprising the steps of:
a) providing from 5 to 95% gum base, 10 to 90% of a bulking agent, and 0.1 to 10% of a flavoring agent, at least one of said bulking and flavoring agents also being an Alitame degradation agent;
b) agglomerating Alitame with an agent which slows Alitame degradation so that at least 60% of an original quantity of Alitame formulated in the gum remains after 8 weeks of storage at 29 °C (85 °F), excepting that the Alitame is not blended with Acesulfame K prior to agglomeration and the agglomerated Alitame is not coated with zein; and
c) intimately mixing the coated Alitame, the gum base, bulking agent and flavouring agent to make a chewing gum composition.

21. A method of making a chewing gum with Alitame comprising the steps of:
a) providing from 5 to 95% gum base, 10 to 90% of a bulking agent, and 0.1 to 10% of a flavouring agent, at least one of said bulking and flavouring agents also being an Alitame degradation agent;
b) absorbing Alitame in an agent which slows Alitame degradation so that at least 60% of an original quantity of Alitame formulated in the gum remains after 8 weeks of storage of 29 °C (85 °F), excepting that the Alitame is not blended with Acesulfame K prior to being absorbed in an agent and the absorbed Alitame is not coated with zein; and
c) intimately mixing the coated Alitame, the gum base, bulking agent and flavouring agent to make a chewing gum composition.

Patentansprüche

1. Eine Kaugummizusammensetzung, die in inniger Mischung umfasst,
a) 5 bis 95% einer Kaugummibasis;
b) 10 bis 90% eines Füllmittels;
c) 0,1 bis 10% eines Geschmacksstoffes; und

d) beschichtetes Alitam, wobei wenigstens eines von den Kaugummiinhaltsstoffen, Füllmitteln oder Geschmacksstoffen auch ein Alitamabbaumittel ist, und wobei das Alitam ausreichend beschichtet ist, um den Alitamabbau aufgrund des Abbaumittels so zu verlangsamen, daß wenigstens 60% einer ursprünglichen Menge an Alitam in dem Kaugummi nach 8 Wochen der Lagerung bei 29 °C (85 °F) zurückbleibt, mit der Ausnahme, daß das beschichtete Alitam vor der Beschichtung nicht mit Acesulfam K gemischt wird, und das beschichtete Alitam nicht mit Zein beschichtet wird.

2. Die Kaugummizusammensetzung nach Anspruch 1, wobei das Alitam 0,005 bis 0,10% der gesamten Kaugummizusammensetzung umfasst.

3. Die Kaugummizusammensetzung nach Anspruch 1 oder Anspruch 2, wobei das Kaugummi ein zuckerfreies Kaugummi ist.

4. Die Kaugummizusammensetzung nach einem der Ansprüche 1 bis 3, wobei das Füllmittel einen Zuckeralkohol, ausgewählt aus Sorbitol, Mannitol, Xylitol, Maltitol, hydrierten Stärkehydrolysaten und Mischungen davon, umfasst.

5. Das Kaugummi nach einem der Ansprüche 1 bis 4, wobei das Alitam mit einem Material beschichtet wird, das aus Acrylpolymeren, Carboxyvinylpolymeren, Polyamiden, Polystyrol, Polyvinylacetat, Polyvinylacetatphthalat Polyvinylpyrrolidon,

6. Die Kaugummizusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Alitam mit einem Material beschichtet wird, das aus Agaralginaten, Guargummi, Tragacanthgummi, Carrageena und Xanthangummi ausgewählt wird.

7. Die Kaugummizusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Alitam mit einem Material beschichtet wird, das ein Cellulosederiverat umfaßt, das aus Ethylcellulose, Methylcellulose, Natriumhydroxymethylcellulose, Hydroxypropylmethylcellulose und modifizierter Stärke ausgewählt wird.

8. Die Kaugummizusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Alitam mit einem Material beschichtet wird, das aus Schellack und Gelatine ausgewählt wird.

9. Ein Verfahren zur Herstellung eines Kaugummis, das Alitam enthält, das umfaßt die Schritte von:
a) Bereitstellen von 5 bis 95% Kaugummibasis, 10 bis 90% eines Füllmittels und 0,1 bis 10% eines Geschmackstoffes, wobei wenigstens eines dieser Füll- und Geschmacksmittel auch ein Abbaumittel für Alitam ist;
b) Beschichten einer Menge von Alitam mit einem Beschichtungsmaterial, das den Alitamabbau auf Grund des Alitamabbaumittels so verlangsamt, daß wenigstens 60% einer ursprünglichen in das Gummi gegebenen Menge an Alitam nach 8 Wochen der Lagerung bei 29 °C (85 °F) zurückbleibt, mit der Ausnahme, daß das beschichtete Alitam vor dem Beschichten nicht mit Acesulfam K gemischt wird, und daß das beschichtete Alitam nicht mit Zein beschichtet wird, und
c) inniges Mischen des beschichteten Alitams, der Kaugummibasis, des Füllmittels und des Geschmacksstoffes, um eine Kaugummizusammensetzung herzustellen.

10. Das Verfahren nach Anspruch 9, wobei die Menge an Alitam, das zu den anderen Inhaltsstoffen zugegeben wird, zwischen 0,005 bis 0,10% der gesamten Kaugummizusammensetzung beträgt.

11. Das Verfahren nach Anspruch 9 oder 10, wobei das Kaugummi ein zuckerfreies Kaugummi ist.

12. Das Verfahren nach einem der Ansprüche 9 bis 11, wobei das Füllmittel einen Zuckeralkohol, ausgewählt aus Sorbitol, Mannitol, Xylitol, Maltitol, hydrierten Stärkehydrolysaten und Mischungen davon, umfasst.

13. Das Verfahren nach einem der Ansprüche 9 bis 12, wobei das Alitam mit einem Material beschichtet wird, das aus Acrylpolymeren, Carboxyvinylpolymeren, Polyamiden, Polystyrol, Polyvinylacefat, Polyvinylacetatphthalat Polyvinylpyrrolidon, und Copolymeren davon ausgewählt wird.

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14. Das Verfahren nach einem der Ansprüche 9 bis 12, wobei das Beschichtungsmaterial aus Agaralginaten. Guargummi, Tragacanthgummi, Carrageena und Xanthangummi ausgewählt wird.

15. Das Verfahren nach einem der Ansprüche 9 bis 12, wobei das Beschichtungsmaterial ein Cellulosederiverat umfaßt, das aus Ethylcellulose, Methylcellulose, Natriumhydroxymethylcellulose, Hydroxypropylmethylcellulose und modifizierten Stärken ausgewählt wird.

16. Das Verfahren nach einem der Ansprüche 9 bis 12, wobei das Beschichtungsmaterial aus Schellack und Gelatine ausgewählt wird.

17. Das Verfahren nach einem der Ansprüche 9 - 16, wobei der Schritt zum Beschichten von Alitam umfaßt:
a) Mischen einer Menge von Alitam mit einem verkapselnden Material;
b) Agglomerieren des verkapselten Alitams.

18. Das Verfahren nach einem der Ansprüche 9 - 16, wobei der Beschichtungsschritt von Alitam umfasst:
a) Mischen einer Menge von Alitam mit einem Lösungsmittel zum Sprühtrocknen und einem verkapselnden Material; und
b) Sprühtrocknen der Mischung auf solche Weise, um das Alitam zu verkapseln.

19. Das Verfahren nach einem der Ansprüche 9 - 16, wobei der Schritt zum Beschichten des Alitams das Flüssigbettbeschichten einer Menge von Alitam mit einem verkapselnden Material umfaßt, das in einem Lösungsmittel aufgelöst oder dispergiert ist.

20. Ein Verfahren zur Herstellung eines Kaugummis, das Alitam enthält, das umfaßt die Schritte von:
a) Bereitstellen von 5 bis 95% Kaugummibasis, 10 bis 90% eines Füllmittels und 0,1 bis 10% eines Geschmackstoffes, wobei wenigstens eines dieser Füll- und Geschmacksmittel auch ein Abbaumittel für Alitam ist;
b) Agglomerieren einer Menge von Alitam mit einem Mittel, das den Alitamabbau so verlangsamt, daß wenigstens 60% einer ursprünglichen in das Gummi gegebenen Menge an Alitam nach 8 Wochen der Lagerung bei 29 °C (85 °F) zurückbleibt, mit der Ausnahme, daß das Alitam vor dem Agglomerieren nicht mit Acesulfam K gemischt wird, und daß das agglomerierte Alitam nicht mit Zein beschichtet wird, und
c) inniges Mischen des beschichteten Alitams, der Kaugummibasis, des Füllmittels und des Geschmacksstoffes, um eine Kaugummizusammensetzung herzustellen.

21. Ein Verfahren zur Herstellung eines Kaugummis, das Alitam enthält, das umfaßt die Schritte von:
a) Bereitstellen von 5 bis 95% Kaugummibasis, 10 bis 90% eines Füllmittels und 0,1 bis 10% eines Geschmackstoffes, wobei wenigstens eines dieser Füll- und Geschmacksmittel auch ein Abbaumittel für Alitam ist;
b) Absorbieren einer Menge von Alitam in ein Mittel, das den Alitamabbau so verlangsamt, daß wenigstens 60% einer ursprünglichen in das Gummi gegebenen Menge an Alitam nach 8 Wochen der Lagerung bei 29 °C (85 °F) zurückbleibt, mit der Ausnahme, daß das Alitam, bevor es in ein Mittel absorbiert wird, nicht mit Acesulfam K gemischt wird, und daß das absorbierte Alitam nicht mit Zein beschichtet wird, und
c) inniges Mischen des beschichteten Alitams, der Kaugummibasis, des Füllmittels und des Geschmacksstoffes, um eine Kaugummizusammensetzung herzustellen.

Revendications

1. Composition de gomme à mâcher comprenant un mélange intime de :
a) 5 à 95 % de base de gomme ;
b) 10 à 90 % d'agent de charge ;
c) 0,1 à 10 % d'agent aromatisant ; et
d) de l'alitame enrobé ;
dans laquelle au moins un desdits ingrédients base de gomme, agent de charge ou agent aromatisant est aussi un agent de décomposition de l'alitame, et dans laquelle l'alitame est suffisamment enrobé pour ralentir sa décomposition qui est due à l'agent de décomposition, de sorte qu'au moins 60 % de

la quantité originelle d'alitame de la gomme à mâcher subsistent après 8 semaines de stockage à 29 °C (85 °F), sauf que l'alitame enrobé n'est pas mélangé avec de l'acésulfame K avant l'enrobage et qu'il n'est pas enrobé avec de la zéine.

2. Composition de gomme à mâcher selon la revendication 1, dans laquelle l'alitame constitue de 0,005 à 0,10 % de la composition totale de la gomme.

3. Composition de gomme à mâcher selon la revendication 1 ou 2, dans laquelle la gomme à mâcher est une gomme à mâcher sans sucre.

4. Composition de gomme à mâcher selon l une quelconque des revendications précédentes, dans laquelle l'agent de charge comprend un alcool de sucre choisi dans l'ensemble constitué par le sorbitol, le mannitol, le xylitol, le maltitol, des hydrolysats hydrogénés d'amidon, et des mélanges de ceux-ci.

5. Composition de gomme à mâcher selon l'une quelconque des revendications précédentes, dans laquelle l'alitame est enrobé avec un matériau choisi dans l'ensemble constitué par les polymères acryliques, les polymères carboxyvinyliques, les polyamides, le polystyrène, l'acétate de polyvinyle, l'acétophtalate de polyvinyle, la polyvinylpyrrolidone, et des copolymères de ceux-ci.

6. Composition de gomme à mâcher selon l'une quelconque des revendications 1 à 4, dans laquelle l'alitame est enrobé avec un matériau choisi dans l'ensemble constitué par des alginates d'agar, la gomme de guar, la gomme adraganthe, un carraghénane et la gomme de xanthane.

7. Composition de gomme à mâcher selon l'une quelconque des revendications 1 à 4, dans laquelle l'alitame est enrobé avec un matériau qui comprend un dérivé cellulosique choisi dans l'ensemble constitué par l'éthylcellulose, la méthylcellulose, l'hydroxyméthylcellulose sodique, l'hydroxypropylméthylcellulose et des amidons modifiés.

8. Composition de gomme à mâcher selon l'une quelconque des revendications 1 à 4, dans laquelle l'alitame est enrobé avec un matériau choisi dans l'ensemble constitué par le shellac et la gélatine.

9. Procédé de préparation d'une gomme à mâcher contenant de l'alitame, comprenant les étapes consistant à :

a) fournir de 5 à 95 % de base de gomme, 10 à 90 % d'agent de charge et 0,1 à 10 % d'agent aromatisant, au moins l'agent de charge ou l'agent aromatisant étant aussi un agent de décomposition de l'alitame ;

b) enrober une quantité d'alitame avec un matériau d'enrobage qui ralentit la décomposition de l'alitame, qui est due à l'agent de décomposition de l'alitame, de sorte qu'au moins 60 % de la quantité originelle d'alitame qui est contenue dans la gomme subsistent après 8 semaines de stockage à 29 °C (85 °F), sauf que l'alitame enrobé n'est pas mélangé avec de l'acésulfame K avant l'enrobage et qu'il n'est pas enrobé avec de la zéine ; et

c) mélanger intimement l'alitame enrobé, la base de gomme, l'agent de charge et l'agent aromatisant, pour obtenir une composition de gomme à mâcher.

10. Procédé selon la revendication 9, où la quantité d'alitame ajouté aux autres ingrédients vaut entre 0,005 et 0,10 % de la composition totale de la gomme.

11. Procédé selon la revendication 9 ou 10, où la gomme à mâcher est une gomme à mâcher sans sucre.

12. Procédé selon l'une quelconque des revendications 9 à 11, où l'agent de charge comprend, en outre, un alcool de sucre choisi dans l'ensemble constitué par le sorbitol, le mannitol, le xylitol, le maltitol, des hydrolysats hydrogénés d'amidon, et des mélanges de ceux-ci.

13. Procédé selon l'une quelconque des revendications 9 à 12, où le matériau d'enrobage est choisi dans l'ensemble constitué par les polymères acryliques, les polymères carboxyvinyliques, les polyamides, le polystyrène, l'acétate de polyvinyle, l'acétophtalate de polyvinyle, la polyvinylpyrrolidone, et des copolymères de ceux-ci.

14. Procédé selon l'une quelconque des revendications 9 à 12, où le matériau d'enrobage est choisi dans l'ensemble constitué par des alginates d'agar, la gomme de guar, la gomme adraganthe, un carraghénane et la gomme de xanthane.

15. Procédé selon l'une quelconque des revendications 9 à 12, où le matériau d'enrobage comprend un dérivé cellulosique choisi dans l'ensemble constitué par l'éthylcellulose, la méthylcellulose, l'hydroxyméthylcellulose sodique, l'hydroxypropylméthylcellulose et des amidons modifiés.

16. Procédé selon l'une quelconque des revendications 9 à 12, où le matériau d'enrobage est choisi dans l'ensemble constitué par le shellac et la gélatine.

17. Procédé selon l'une quelconque des revendications 9 à 16, où l'étape d'enrobage de l'alitame comprend :
a) le mélange d'une quantité d'alitame avec un matériau d'encapsulation ; et
b) l'agglomération de l'alitame encapsulé.

18. Procédé selon l'une quelconque des revendications 9 à 16, où l'étape d'enrobage de l'alitame comprend :
a) le mélange d'une quantité d'alitame avec un solvant de séchage par pulvérisation et un matériau d'encapsulation ; et
b) le séchage par pulvérisation du mélange de manière à encapsuler l'alitame.

19. Procédé selon l'une quelconque des revendications 9 à 16, où l'étape d'enrobage de l'alitame comprend l'enrobage en lit fluidisé d'une quantité d'alitame avec un matériau d'encapsulation dissous ou dispersé dans un solvant.

20. Procédé de préparation d une gomme à mâcher contenant de l'alitame, comprenant les étapes consistant à :
a) fournir de 5 à 95 % de base de gomme, 10 à 90 % d'agent de charge et 0,1 à 10 % d'agent aromatisant, au moins ledit agent de charge ou ledit agent aromatisant étant aussi un agent de décomposition de l'alitame ;
b) agglomérer l'alitame avec un agent qui ralentit la décomposition de l'alitame, de sorte qu'au moins 60 % de la quantité originelle d'alitame qui est contenue dans la gomme subsistent après 8 semaines de stockage à 29 °C (85 °F), sauf que l'alitame n'est pas mélangé avec de l'acésulfame K avant l'agglomération et que l'alitame aggloméré n'est pas enrobé avec de la zéine ; et
c) mélanger intimement l'alitame enrobé, la base de gomme, l'agent de charge et l'agent aromatisant, pour obtenir une composition de gomme à mâcher.

21. Procédé de préparation d'une gomme à mâcher contenant de l'alitame, comprenant les étapes consistant à :
a) fournir de 5 à 95 % de base de gomme, 10 à 90 % d'agent de charge et 0,1 à 10 % d'agent aromatisant, au moins ledit agent de charge ou ledit agent aromatisant étant aussi un agent de décomposition de l'alitame ;
b) faire absorber l'alitame dans un agent qui ralentit la décomposition de l'alitame, de sorte qu'au moins 60 % de la quantité originelle d'alitame qui est contenue dans la gomme subsistent après 8 semaines de stockage à 29 °C (85 °F), sauf que l'alitame n'est pas mélangé avec de l'acésulfame K avant d'être absorbé dans ledit agent et que l'alitame absorbé n'est pas enrobé avec de la zéine ; et
c) mélanger intimement l'alitame enrobé, la base de gomme, l'agent de charge et l'agent aromatisant, pour obtenir une composition de gomme à mâcher.

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(54) Stable, spray-dried composition in a carbohydrate substrate and process for obtaining said composition

(57) The invention relates to a moisture and oxygen stable spray-dried composition comprising at least one active compound encapsulated in a carbohydrate matrix, which matrix is characterised by

- 40 to 80 wt.% high molecular weight film forming carbohydrate;
- 10 to 30 wt.% mono, di and trisaccharides; and
- 10 to 30 wt.% maltodextrin.

based on the total weight of the carbohydrate matrix. The active compound to be encapsulated in the carbohydrate matrix can be selected from the group consisting of flavourants, fragrances, pharmaceuticals and wash-active components.

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Description

[0001] The invention relates to a moisture and oxygen stable spray-dried composition comprising at least one active compound like a moisture or oxygen sensitive flavourant, a fragrance or another type of a moisture or oxygen sensitive compound e.g. a pharmaceutical. Further, the invention relates to a process for fixing volatile flavourants, fragrances or other volatile and moisture or oxygen sensitive compounds in an amorphous matrix.

[0002] With regard to the field of flavours it is noted that for instance efforts have been made to give the consumer a fresher tasting reconstitutable beverage mix by using certain natural, natural identical or artificial volatile compounds for improving the consumer's taste perception. Unlike liquid systems which usually retain flavourants without adverse stability problems, dry comestible beverage mixes are often lacking in flavour or have off-flavours due to poor storage stability. A fresh tasting, reconstituted beverage would increase the consumer's perception of freshness which is of paramount importance.

[0003] Such compounds as coffee aroma, esters, acetaldehyde, various essential oils and sulphur compounds, augment or enhance the taste perception of convenience foods. Dry comestible mix systems present special problems when one tries to introduce volatile or aromatic flavourants therein. For example, such materials escape through and from the mix, or react so as to degrade or oxidize into compounds which are recognized to be less desirable. Therefore, there has been a long-standing need to fix by encapsulation, and prevent the escape of volatiles within a "powdered-mix" comestible and prevent oxidation thereof. Moreover, the process for fixing a volatile must produce a product which is easily reconstitutable and is capable of holding the fix over prolonged periods and under adverse storage conditions.

[0004] A major problem inherent in fixing aromatics in food allowed substrates is the fact that those fixation substrates display idiosyncratic fixation characteristics. The substrate media may be sensitive to moisture, react with the entrained volatile or produce flavour off-notes. Carbohydrates as a class offer a food-acceptable substrate in which volatiles and aromatics have been fixed. However, most water-soluble carbohydrate substrates are hygroscopic and will not reliably hold the fix for long periods. In view of the foregoing, there is a recognized need for an amorphous moisture-stable, water-soluble, food-approved substrate to encapsulate aromatic or volatile flavourants.

[0005] Where flavours, such as essential oils, are not protected by an antioxidant, even further problems of off-flavour development are encountered due to oxidation caused by the inability of the carbohydrate matrix to protect the flavour from oxygen.

[0006] EP 0,550,067 B1 relates to a method for encapsulating oils such as fragrance and flavouring oils in a water-sensitive cellular solid matrix, comprising drying an aqueous emulsion containing (a) the oil to be encapsulated, (b) a non-crosslinked lipophilically modified starch that undergoes crosslinking under the drying conditions and (c) a polyhydroxy compound that forms with the polysaccharide material a continuous aqueous phase in which the oil is dispersible as a discontinuous phase. The oil (a) which typically contains a conventional antioxidant like butylated hydroxy toluene is typically encapsulated in the dried carbohydrate matrix in an amount from 5 to 80%, preferably at least 65% by weight of the oil and matrix combination. The modified starch (b) is in principle an ungelatinised starch acid ester of a substituted dicarboxylic acid, and the polyhydroxy compound (c) are polyalcohols like glycerol, mannitol etc., and sugars including mono, di and trisaccharides like glucose, fructose, maltose, sucrose, and raffinose.

[0007] US 5,102,682 A relates to a dry flavoured powdered food mix comprising at least 20% crystalline sucrose, at least 10% crystalline fructose, 1-8% crystalline food acid, flavour and anti-caking agent, wherein all components are present in a free, unbound state and wherein the crystalline fructose compound contains less than 10% by weight of particles smaller than 150 µm. As indicated in said US 5,102,682 the fructose and sucrose content of the food mix can range from 10-60% and 20-80% respectively, and the combined weight of fructose and sucrose will usually be at least 40%, and for soft drink mixes such as fruit-flavoured beverage mixes will typically be at least 90%, usually about 95% or more of the mix.

[0008] The flavours suitable for use in the food mix can be spray-dried flavours fixed in a carbohydrate matrix consisting of either maltodextrin or a combination of maltodextrin and a modified starch. According to said US 5,102,682 typical spray-dried flavours contain 30-60% modified food starch and 30-60% maltodextrin and flavourant.

[0009] EP 0,426,428 B1 relates to a delivery system for flavours and sweeteners and to a process for its preparation, which system has use in a variety of products including comestibles such as chewing gum, food products etc. More in particular EP 0,426,428 B1 relates to a process for producing a flavour delivery system prepared from a spray-dried emulsion of

(a) from 0.1 to 40 wt.% of a flavour oil,
(b) from 0.5 to 30 wt.% of a sweetener and
(c) from 30 to 80 wt.% of a film-forming polymer coating component, all amounts are based on the total weight of the delivery system.

[0010] Suitable sweeteners to be encapsulated in the delivery system include natural and artificial high intensity sweeteners selected from amino acid-based sweeteners, dipeptide sweeteners, glycyrrhizin, saccharin and its salts, acesulfame salts, cyclamates, steviosides, talin, sucralose, dihydrochalcone compounds and mix-

tures thereof. However, according to EP 0,426,428 B1 it is also possible to use sweeteners in addition to those that are already included in the delivery system. Such additional sweeteners may be selected from e.g. sucrose, glucose, dextrose, invert sugar, fructose etc.

[0011] Further, US 5,124,162 A is directed to a moisture and oxygen stable spray-dried fixed flavour comprising a flavourant encapsulated in a carbohydrate matrix consisting of 22 to 50%, preferably 22 to 45% mono and disaccharides, wherein at least 50% of the mono and disaccharides is maltose, 25 to 60%, preferably 25 to 50% maltodextrin, and 10 to 40%, preferably 10 to 35% high molecular weight film forming carbohydrate.

[0012] With regard to the field of perfumes and perfumed products it is referred to WO 94/19449 indicating the detrimental impact of high humidity conditions on products based on a water sensitive matrix e.g. a starch matrix and a fragrance or a wash-active component encapsulated therein. This type of encapsulates may be added to a number of articles to be perfumed including laundry powder, soap and machine dishwash powder. Apparently the problem encountered in WO 94/19449 is solved by a composition comprising (a) a substance encapsulated within a water-sensitive matrix so as to be releasable upon contact with water or aqueous solutions, mixed with (b) particles of inorganic carrier material carrying a poorly water-soluble oil, such that the composition is stable at high relative humidity. Examples of substances encapsulated in the water-sensitive matrix are a perfume, flavour, a cosmetic ingredient or organometallic complexes e.g. a bleaching agent, bleach activator or bleach catalyst.

[0013] Summarizing the prior art it is noted that the most familiar reference is considered US 5,124,162 A. Therein, it is stated that a moisture and oxygen stable spray-dried composition can be obtained if -next to the other two components of the carbohydrate matrix- at least 50% of the mono and disaccharide component is maltose. Further, it is indicated in US 5,124,162 A (column 4, lines 19-23) that certain film forming carbohydrates like gum arabic and waxy starches present "leaky" substrates, which will not retain entrapped volatile flavourants.

[0014] Surprisingly, it has now been found that in spite of the above-mentioned prejudice stated in the most familiar reference US 5,124,162 A, a moisture and oxygen stable spray-dried composition could be obtained by using a carbohydrate matrix comprising a rather high amount of 40 to 80 wt.% high molecular weight film forming carbohydrate in combination with 10 to 30 wt.% mono, di and trisaccharides and 10 to 30 wt.% maltodextrin, based on the total weight of the carbohydrate matrix.

[0015] Therefore, the invention relates to a moisture and oxygen stable spray-dried composition comprising at least one active compound encapsulated in a carbohydrate matrix which matrix is characterized by

- 40 to 80 wt.% high molecular weight film forming carbohydrate;
- 10 to 30 wt.% mono, di and trisaccharides; and
- 10 to 30 wt.% maltodextrin

based on the total weight of the carbohydrate matrix.

[0016] More in particular the carbohydrate matrix includes from 45 to 70 wt.%, preferably from 50 to 60 wt. % high molecular weight film forming carbohydrate. Suitable film forming carbohydrates are film forming gums, pectins, alginates, mucilages and mixtures thereof. Preferably the film forming carbohydrates are selected from gum arabic, gum acacia, tragacanth, karaya, ghatti, agar, alginates, carrageenans, fucellan, psyllium and mixtures thereof or from gelatin, dextran, xanthan, curdlan, cellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, carboxymethyl cellulose, low methoxy pectin, propylene glycol alginate and mixtures thereof.

[0017] Most preferably the film forming agents are film forming gums, hydrocolloids and lipophilically modified starches. Examples of gums are gum arabic and gum acacia. Examples of suitably chemically modified starches are Capsul® and N-Lok (National Starch). Of course, also mixtures of film forming carbohydrates can be used in the spray-dried compositions according to the invention.

[0018] Another component of the carbohydrate matrix according to the invention are the mono, di and trisaccharides, which are used in an amount of 10 to 30 wt. %, preferably 15-25 wt.%, based on the total weight of the carbohydrate matrix. Illustrative examples of mono, di and trisaccharides are glucose, fructose, maltose, sucrose, raffinose and materials, having a high content of such sugars like fruit juice solids. Preferably, at least 50 wt.% of the mono, di and trisaccharide material is a disaccharide as a high amount of monosaccharide may result in a somewhat sticky product whereas a high amount of trisaccharide may lead to a product more prone to oxidation. In a preferred embodiment according to the invention the mono, di and trisaccharide material is sucrose.

[0019] The carbohydrate matrix according to the invention further includes 10 to 30 wt.%, preferably 10 to 25 wt.% maltodextrin. The maltodextrin will preferably have a dextrose equivalent (DE) in the range of 1 to 25, most preferably in the range of 10 to 20. A variety of maltodextrins meeting the above requirements are readily available commercially, including maltodextrins from e.g. tapioca, maize and potato..

[0020] The carbohydrate matrix may be softened by the incorporation of up to 5 wt.% of an edible polyol such as glycerol, preferably 1 to 3 wt.%, based on the carbohydrate matrix. Also other components like anti-foam agents in an amount of up to 0.2 ‰ may be added.

[0021] The active compound to be encapsulated in the carbohydrate matrix can be selected from the group consisting of flavourants, fragrances, pharmaceuticals

and wash-active components.

[0022] Flavourants are well-known in the art and are mentioned, e.g., in S. Arctander, Perfume and Flavor Materials of Natural Origin (Elisabeth, N.J., USA, 1996), in T.E. Furia et al, CRC Fenaroli's Handbook of Flavor Ingredients, 2nd Ed. (Cleveland, CRC Press Inc., 1975), and in H.B. Heath, Source Book of Flavors (The Avi Publishing Company Inc., Westport, Connecticut, 1981).

[0023] Fragrances and mixtures thereof which can be used for the preparation of perfumed articles are e.g. naturally occurring products such as essential oils, absolutes, resinoids, resins, concretes etc., natural, nature identical and artificial fragrances, such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitriles etc., covering saturated and unsaturated compounds, aliphatic, carbocyclic and heterocyclic compounds, for instance as disclosed in S. Arctander (loc.cit.).

[0024] Examples of fragrances which may be used within the scope of the invention are: geraniol, geranyl acetate, linalool, linalyl acetate, tetrahydrolinalool, citronellol, citronellyl acetate, dihydro myrcenol, dihydro myrcenyl acetate, tetrahydro myrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, 2-phenylethanol, 2-phenylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethylbenzyl carbinol, trichloromethylphenylcarbinyl acetate, p-tert. butylcyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, α-hexyl-cinnamaldehyde, 2-methyl-3-(p-tert.butylphenyl)-propanal, 2-methyl-3-(p-isopropyl phenyl)-propanal, 3-(p-tert.butylphenyl)-propanal, tricyclodecenyl acetate, tricyclodecenyl propionate, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene carbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexene carbaldehyde, 4-acetoxy-3-pentyl-tetrahydropyran, 3-carboxymethyl-2-pentyl-cyclopentane, 2-n-heptylcyclopentanone, 3-methyl-2-pentyl-2-cyclopentanone, n-decanal, n-dodecanal, dec-9-en-1-ol, phenoxy-ethyl isobyutyrate, phenylacetaldehyde dimethylacetal, phenylacetaldehyde diethylacetal, geranyl nitrile, citronellyl nitrile, cedryl acetate, 3-isocamphyl cyclohexanol, cedrylmethyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropine, coumarin, eugenol, vanillin, diphenyl oxide, hydroxy citronellal, ionones, methyl ionones, isomethyl ionones, irones, cis-3-hexenol and esters thereof, indan musk fragrances, tetralin musk fragrances, isochroman musk frangrances, macrocyclic ketones, macrolactone musk fragrances, ethylene brassylate, aromatic nutri-musk frangrances.

[0025] The fragrance comprising spray-dried products according to the invention may be used successfully in perfumed articles. Examples of such perfumed articles are: soap, bath products, washing agents, dish washing and cleaning agents, pommanders, candles, cosmetics such as creams, ointments, body deodorant sticks and antiperspirant sticks.

[0026] Also pharmaceuticals and wash-active components which are prone to humidity or oxygen can be used as active compound to be encapsulated in the carbohydrate matrix according to the invention.

[0027] A major application of the invention is related to the field of flavours. In this respect it is noted that the final spray-dried product according to the invention is capable of protecting and retaining 5 to 40 wt.% or even more, preferably 20 to 30 wt.% flavourant as active compound, depending on the type of flavourant and based on the total weight of the flavour. Examples of flavourants, in particular aromatic or volatile flavourants, to be encapsulated in the carbohydrate matrix according to the invention are for instance essential oils, like citrus oil, e.g. lemon oil, orange oil, grapefruit oil and other volatile flavourants, like bakery and savoury flavourants. Also other types of active compounds as indicated above can be encapsulated in the carbohydrate matrix according to the invention in an amount of 5-40 wt.% or more, preferably 20-30 wt.%, based on the total weight of the composition.

[0028] A further aspect of the invention is embodied by a process for producing the moisture and oxygen stable composition, comprising the steps of

a) forming an aqueous carbohydrate solution containing a carbohydrate mixture consisting of 40 to 80 wt.% high molecular weight film forming carbohydrate(s), 10 to 30 wt.% mono, di and trisaccharide (s), and 10 to 30 wt.% maltodextrin(s),

b) incorporating at least one active compound defined above into the solution of step (a), and

c) spray-drying the aqueous solution of step (b) using an outlet temperature of 100°C or less to obtain a stable product encapsulated therein the active compound. In general, the procedure of spray-drying involves the following. At first a solution of the product one wishes to make is prepared. The term solution is understood to mean mixtures of solutes and solvents encompassing such mixtures as emulsions or dispersions. The solution is fed into an atomizer which creates a fine mist, composed of regular-sized droplets. The misted solution is introduced, usually through the top of a drying tower or chamber into the spraydryer. Heated air is fed into the chamber so that as the droplets fall from the top of the chamber evaporation and drying of the aqueous liquid phase respectfully occurs. The product is collected from an outlet port. Examples of spray-drying apparatus are the Anhydro Dryers (manufactured by Anhydro Corp. of Attleboro Falls, Mass. U. S.A.) or the Niro Dryer (manufactured by Niro Atomizer Ltd, Copenhagen, Denmark).

[0029] More in particular the combination of carbohydrate materials is dissolved in water to form an aqueous solution with the temperature being maintained at around 10°C to 90°C. In the case of a highly volatile substance the solution is allowed to cool to about the boiling point of the substance or below. The active compound,

for instance a volatile or aromatic flavourant is then added to the solution, the solution being preferably maintained at from 10°C to 50°C. The solution is then spray-dried in an atmospheric spraydryer wherein the inlet temperature is typically about 140°C to 210°C and the outlet temperature typically 70°C to 100°C. The resultant moisture-stable product has an excellent retention of volatiles over time and a prolonged shelf life without unacceptable oxidation. No antioxidant is added or made part of the final product.

[0030] The invention is elucidated by means of the following examples and the storage properties of the spray-dried products are illustrated by means of the Figures 1 and 2.

Fig. 1 illustrates the accelerated shelf life test of

- a product according to the prior art based on 25 wt.% orange flavourant (QL 06830 marketed by Quest International, the Netherlands) and 75 wt.% of a carbohydrate matrix consisting of 50 wt.% Capsul® and 50 wt.% maltodextrin (DE 20), and
- a product according to the invention based on 25 wt.% orange flavourant (QL 06830) and 75 wt.% of a carbohydrate matrix consisting of 50 wt.% Capsul®, 23 wt.% maltodextrin (DE 20), 25 wt.% sucrose and 2 wt.% glycerol.

More in particular the X-axis represents the time in weeks, and the Y-axis represents the amount of carvone in wt.%, formed from the spray-dried products due to oxidation of the limonene component of the used orange flavourant during the accelerated shelf life test at 40°C and at a relative humidity (RH) of 30%.

Fig. 2 illustrates the accelerated shelf life test of

- the product according to the prior art shown in Fig. 1, and
- a product according to the invention based on 25 wt.% orange flavourant (QL 06830) and 75 wt.% of a carbohydrate matrix consisting of 60 wt.% gum acacia, 20 wt.% maltodextrin (DE 10) and 20 wt.% sucrose.

More in particular the X-axis represents the time in weeks, and the Y-axis represents the amount of carvone in wt.%, formed from the spray-dried products due to oxidation of the limonene component of the used orange flavourant during the accelerated shelf life test at 40°C and at a relative humidity (RH) of 50%.

Example 1

[0031] The following two formulations were prepared by dissolving or dispersing the components indicated below

(a) 500 g of a carbohydrate matrix comprising 50 wt.% (250 g) Capsul® and 50 wt.% (250 g) maltodextrin (DE 20) being a carbohydrate matrix used for marketed products; and
(b) 500 g of a carbohydrate matrix consisting of 50 wt.% (250 g) Capsul®, 23 wt.% (115 g) maltodextrin (DE 20), 25 wt.% (125 g) sucrose and 2 wt.% (10 g) glycerol being a carbohydrate matrix according to the invention

under stirring in 600 g warm water of 80°C for 30 minutes. Then the mixture was cooled to 20°C. An orange flavourant (QL 06830) without any antioxidant preservative was added in an amount of 25 wt.% on total dry solids (166 g) under stirring and the prepared feed was homogenised using a Ultra Turrax T50 at 10,000 rpm for about 3 minutes. The homogenised feed was spray-dried in a NIRO MOBIL MINOR SPRAY DRYER using a rotary wheel atomiser at 20,000 rpm. Inlet air temperature was kept at 190°C, resulting in an outlet temperature in the range of 90°C.

[0032] As apparent from Fig. 1, the product according to the invention had an excellent stability and a desired long storage life compared to the prior art product. More in particular the storage time of 8 weeks in the accelerated shelf life test at 40°C and a RH of 30% corresponds to a storage time of about one year at room temperature (20°C) and a RH of 30%.

Example 2

[0033] The following two formulations were prepared by dissolving or dispersing the components indicated below

(a) 500 g of a carbohydrate matrix consisting of 50 wt.% (250 g) Capsul® and 50 wt.% (250 g) maltodextrin (DE 20) being a carbohydrate matrix used for marketed products; and
(b) 316 g of a carbohydrate matrix consisting of 60 wt.% (190 g) gum acacia, 20 wt.% (63 g) maltodextrin (DE 10) and 20 wt.% (63 g) sucrose being a carbohydrate matrix according to the invention

under stirring in 600 g warm water of 60°C for 30 minutes. Then the mixture was cooled to 20°C. An orange flavourant (QL 06830) without any antioxidant preservative was added in an amount of 25 wt.% on total dry solids (166 g for formulation (a) and 105 g for formulation (b)) under stirring and the prepared feed was homogenised using a Ultra Turrax T50 at 10,000 rpm for about 3 minutes. The homogenised feed was spray-dried in a NIRO MOBIL MINOR SPRAY DRYER using a rotary wheel atomiser at 20,000 rpm. Inlet air temperature was kept at 190°C, resulting in an outlet temperature in the

range of 90°C.

[0034] As apparent from Fig. 2, the product according to the invention had an excellent stability and a desired long storage life compared to the prior art product. More in particular the storage time of 8 weeks in the accelerated shelf life test at 40°C and a RH of 50% corresponds to a storage time of about one year at room temperature (20°C) and a RH of 50%.

Claims

1. A moisture and oxygen stable spray-dried composition comprising at least one active compound encapsulated in a carbohydrate matrix, which matrix is characterised by

   - 40 to 80 wt.% high molecular weight film forming carbohydrate;
   - 10 to 30 wt.% mono, di and trisaccharides; and
   - 10 to 30 wt.% maltodextrin

   based on the total weight of the carbohydrate matrix.

2. The spray-dried composition according to claim 1, characterised in that the film forming carbohydrate is present in an amount of 45 to 70 wt.%, preferably 50-60 wt.% based on the total weight of the carbohydrate matrix.

3. The spray-dried composition according to claim 1 or 2, characterised in that the film forming carbohydrate is selected from the group consisting of gum arabic, gum acacia, lipophilically modified starches and mixtures thereof.

4. The spray-dried composition according to any of claims 1-3, characterised in that the mono, di and trisaccharides are present in an amount of 15-25 wt.% based on the total weight of the carbohydrate matrix.

5. The spray-dried composition according to any of claims 1-4, characterised in that at least 50 wt.% of the mono, di and trisaccharide material is a disaccharide.

6. The spray-dried composition according to claim 5, characterised in that the disaccharide is sucrose.

7. The spray-dried composition according to claims 5 or 6, characterised in that 100 wt.% of the mono, di and trisaccharide material is sucrose.

8. The spray-dried composition according to any of claims 1-7, characterised in that the maltodextrin has a dextrose equivalent (DE) in the range of 1 to 25, preferably 10 to 20.

9. The spray-dried composition according to any of claims 1-8, characterised in that the active component encapsulated in the carbohydrate matrix is selected from the group consisting of flavourants, fragrances, pharmaceuticals and wash-active components.

10. The spray-dried composition according to any of claims 1-9, characterised in that the encapsulated active compound is at least one flavourant selected from the group consisting of essential oils, like citrus oil, e.g. lemon oil, orange oil, grapefruit oil, bakery flavourants and savoury flavourants.

11. The spray-dried composition according to any of claims 1-10, characterised in that the encapsulated active compound is present in an amount of 5-40 wt.%, preferably 20-30 wt.%, based on the total weight of the composition.

12. A process for producing a moisture and oxygen stable composition comprising the steps of

    (a) forming an aqueous carbohydrate solution containing a carbohydrate mixture consisting of 40 to 80 wt.% high molecular weight film forming carbohydrate(s), 10 to 30 wt.% mono, di and trisaccharide(s), and 10 to 30 wt.% maltodextrin(s);
    (b) incorporating at least one active compound into the solution of step (a); and
    (c) spray-drying the aqueous solution of step (b) using an outlet air temperature of 100°C or less, to obtain a stable product encapsulated therein the active compound.

13. The process according to claim 12, characterised in that the active compound is selected from the group consisting of flavourants, fragrances, pharmaceuticals and wash-active components.

14. Products comprising the spray-dried composition according to any of claims 1-11 or prepared by the process according to claim 12 or 13.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 3854

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)

A23L
A61K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	3 May 2000	Herrera, S

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 20 3854

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(54) Title: CHEWING GUM CONTAINING GUM TALHA

(57) Abstract

Chewing gums containing gum talha and methods of making such gums are disclosed. In one embodiment, the gum comprises about 5 % to about 95 % gum base, about 0.1 % to about 10 % flavoring agent and gum talha, the gum talha being part of the bulking agent in the gum. The gum talha provides the gum with unique properties, and the gum is non-cariogenic. In another embodiments, the gum talha is codried with sweeteners or coevaporated with a plasticizing syrup to produce unique sweetening ingredients and syrups for gum. The gum talha may also be provided in the form of a rolling compound on the gum, or used with sugars or polyols to form a hard coating for a coated pellet gum.

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CHEWING GUM CONTAINING GUM TALHA

BACKGROUND OF THE INVENTION

The present invention relates to improved compositions of chewing gum. More particularly, the invention relates to improving chewing gum by the use of specific bulking agents in sugar and non-sugar chewing gum products to give improved texture, moisture absorption properties, and improved shelf life properties. The improved chewing gum compositions may also be used in a variety of chewing gum products such as confectionery coated chewing gum products.

In recent years, efforts have been devoted to replace sugar and sugar syrups normally found in chewing gum with other carbohydrates and non-carbohydrates. Non-sugar or sugar-free chewing gum, which is growing in popularity, uses sugar alcohols or polyols to replace sugar and sugar syrups. The most popular polyols are sorbitol, mannitol and xylitol. New polyols are being developed using new technology to replace these polyols. New polyols have various unique properties which can improve the taste, texture and shelf life properties of chewing gum for consumers.

The non-sugar polyols have the advantage of not contributing to dental caries of consumers, as well as being able to be consumed by diabetics. However, all polyols have the disadvantage of causing gastro-intestinal disturbances if consumed in too great of a quantity. Therefore it would be a great advantage to

be able to use a carbohydrate or carbohydrate-like food ingredient for chewing gum that would act as a bulking agent, but not contribute to dental caries nor cause gastro-intestinal disturbances.

One such bulking agent is called gum talha, a natural gum derived from species of plants from the Acacia genus. Gum arabic is a another common natural gum derived from a different species of plants within the Acacia genus. Gum talha is approved for use in food products, including chewing gum, in the U.S. and other countries. Although a carbohydrate, gum talha is a natural gum that does not contribute to dental caries, nor does it cause gastro-intestinal disturbances. Thus, this ingredient's use in chewing gum could be a definite improvement.

The use of liquid and powder gum arabic in chewing gum was disclosed in U.S. Patent No. 3,352,689. It was also disclosed in a non-sweet chewing gum in U.S. Patent No. 5,084,298. As a chewing gum binder, gum arabic was disclosed in U.S. Patent No. 4,271,197 with hydrogenated starch hydrolyzates, in PCT Patent Publication No. W095/08928 with erythritol, and Japanese Patent Publication No. 80-9177 with sorbitol, mannitol, and stevioside. Japanese Patent Publication No. 87-146562 disclosed using gum arabic to make a rice cake-like gum.

The use of gum arabic has been disclosed in various chewing gum or confectionery coating or panning applications. U.S. Patent No. 3,576,663 discloses the use of gum arabic combined with a sucrose coating. U.S. Patent No. 4,317,838, South Africa Patent Publication No. 87-2848, Great Britain Patent Publication No. 2,115,672, and European Patent Publication No. 0 625 311, disclose gum arabic combined with various polyols to make sugarless coatings. In U.S. Patent No. 5,135,761 discloses applying gum arabic

after an emulsifier subcoating. Also, sugarless coatings containing calcium chloride with gum arabic are disclosed in U.S. Patent Nos. 4,681,766 and 4,786,511.

Gum arabic has been used in a wide variety of encapsulation applications. It is commonly used to emulsify and spray dry flavor compositions. European Patent Publication No. 0 545 632 discloses a spray dried flavor composition and European Patent Publication No. 0 455 598 discloses a microencapsulated flavor coated with gum arabic, and gluteraldehyde. U.S. Patent No. 4,576,737 discloses gum arabic encapsulation of volatile liquids. U.S. Patent No. 5,124,162 discloses a citrus oil in maltose and maltodextrin coated with gum arabic. Great Britain Patent Publication No. 1,472,787 discloses a flavor on a gum arabic carrier. Great Britain Patent No. 1,572,536 and PCT Patent Publication No. W095/17104 disclose gum arabic as an encapsulating agent for aspartame. French Patent Publication No. 2,476,986 discloses vitamin C encapsulated with gum arabic.

SUMMARY OF THE INVENTION

The present invention is a method of producing chewing gum with gum talha, as well as the chewing gum so produced. The bulking agent may be added to sucrose-type gum formulations, replacing a small or large quantity of sucrose. The formulation may be a low- or high- moisture formulation containing low or high amounts of moisture-containing syrup. The bulking agent, gum talha, may also be used in low- or non-sugar gum formulations replacing sorbitol, mannitol, other polyols, or carbohydrates. Non-sugar formulations may include low- or high-moisture, sugar-free chewing gums.

The bulking agent, gum talha, may be combined with other bulking agents for use in chewing gum, including but not limited to sucrose, dextrose, fructose, maltose, maltodextrin, xylose, as well as sugar alcohols including but not limited to sorbitol, mannitol, xylitol, maltitol, lactitol, palatinit and hydrogenated starch hydrolyzates such as Lycasin. The bulking agent, gum talha, may be combined in the gum formulation or co-dried or blended with the other bulk sweeteners prior to use in the gum formulation. Co-drying may be done by various methods of spray drying, fluid bed coating, coacervation, and other granulating or agglomerating techniques. The bulking agent, gum talha, may also be combined with high potency sweeteners including, but not limited to, thaumatin, aspartame, acesulfame K, sodium saccharin, glycyrrhizin, alitame, cyclamate, stevioside and dihydrochalcones.

This material, when used as a bulking agent, gives chewing gum an improved texture, an improved shelf life and unique flavor/ sweetness quality. Even though gum talha is a carbohydrate, it is not cariogenic, nor does it cause gastro-intestinal disturbances, giving a highly consumer-acceptable chewing gum product.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Acacia gums, also sometimes referred to as gum arabic, are defined in the pharmacopeias as "the air-hardened gummy exudates flowing naturally or obtained by incision of the trunk and branches of Acacia senegal and other species of African origin." Though there are many Acacia species (some 700), few are able to provide the amounts of gum required for industrial production. Generally, acacia gums are

grown, harvested, and exported by Senegal, Mali, Nigeria, Chad and the Sudan.

Most definitions imply that the main component for acacia gum or gum arabic is from Acacia senegal, which undoubtedly is the most available gum in the commercial producing countries. The next most available gum is from Acacia seyal. This gum is from another species from the genus Acacia and is called gum talha.

Gum talha from Acacia seyal has a slightly different composition compared to gum arabic from gum senegal. Some differences are noted below:

	Gum Arabic	Gum Talha
Optical rotation	26 - 34°	51°
Nitrogen, %	0.27 - 0.39%	0.14%
Equivalent weight	~ 1100	1470
Glucuronic acid, %	12 - 28%	6.5%

Also, differences in component sugar in the structure of the different gums can be seen in the levels of D-Galactose, L-Arabinose, L-Rhammose, D-Glucuronic acid, and 4-0 methyl glucuronic acid.

Because of the differences in gum arabic and gum talha, these gums may function differently when used in various products. Gum talha has less nitrogen, which means it has less protein than gum arabic, and as a result may not have the same emulsifying properties, adhesive properties, or film forming properties as gum arabic. Even though it has a slightly highly equivalent weight, its viscosity is low and can affect its handling and physical characteristics when used in products.

To compensate for some of the differences in physical properties of gum arabic and gum talha, it may be possible to add protein or starches to a gum talha

solution to improve its emulsifying and adhesive properties. Gum arabic and gum talha contain both AGP (arabinogalactan-protein complex) and GP (glycoprotein) but gum talha, having a lower level of protein, has lower amounts of these materials. By increasing the protein level in a gum talha solution, more emulsifying or adhesive properties may result. Typical proteins include gelatin, casein, soy, wheat gluten and zein.

Previous patents have discussed the use of acacia gum in chewing gum that may generally refer to the use of gum arabic. Also acacia gums used in coatings of gum pellets may also refer to the gum arabic materials commonly used with sugar or xylitol gum coatings. On the other hand, gum talha from Acacia seyal has not been previously disclosed in chewing gum formulations or in pellet gum coatings.

Gum talha from Acacia seyal and gum arabic from Acacia senegal are available from ISC (Importers Service Corporation), 233 Suydom Ave., Jersey City, NJ. Both gums are available in crude, granular, powder, and spray dried forms. All forms of gum talha are included when referring to gum talha herein, including a syrup form produced when gum talha is dissolved in water.

Gum talha may be added to chewing gum in its powder form or may be dissolved in water. Its solubility in water is about 40% at room temperature, but increases with increased temperature. Gum talha may be used in chewing gum as a texture and flavor modifier, bulking agent, and may improve texture, flavor, and shelf life properties. Gum talha may replace solids like sucrose, dextrose or lactose when used in its powder form, or may replace syrups when used in its liquid or syrup form. At levels of about 0.5% to about 25%, gum talha may replace part of the solids in sugar gum or, as a liquid, all or part of the syrup in sugar gum. At higher levels of about 25% to about 70% of the

gum formulation, gum talha may replace all of the solids in a chewing gum formulation.

Unique chewing gum formulations can be obtained when all bulk sweeteners are replaced with gum talha powder and syrup. The low sweetness intensity allows for use of unique flavor combinations. High intensity sweeteners may be added to increase sweetness to obtain a sweetness more typical of chewing gum formulations. The relatively lower solubility of gum talha compared to sucrose could modify the chew texture and shelf life properties significantly. Chewing gum formulations with gum talha may contain a very low amount of moisture in the gum formulation, i.e., below about 2%, or may contain a medium amount of moisture, about 2-5%, and may even be a soft gum formulation containing 5% moisture or more.

Gum talha's unique anti-caries properties suggest it may be used in chewing gum formulations containing non-sugar ingredients. Non-sugar ingredients are alditols such as sorbitol, mannitol, xylitol, lactitol, palatinit (Isomalt), maltitol and hydrogenated starch hydrolyzates. These alditols are used in a variety of combinations to develop unique sugarless chewing gum formulations. Gum talha may be used to replace the individual alditols or combinations of alditols. With partial replacement of one or more alditols, gum talha can be used at levels of about 0.5-25%. If gum talha replaces a large amount or most of the alditols, this level may be about 25% to about 90% of the gum formulation.

Some sugar-free chewing gum formulations contain high levels of glycerin and are very low in moisture, i.e., less than about 2%. Gum talha solids or syrup may replace part or all of the glycerin used in these types of formulations. At higher moisture levels (more than 2%) in sugar-free gum, a liquid

sorbitol (70% sorbitol, 30% water) is used. Gum talha solids or gum talha syrup may replace part or all of the sorbitol liquid. New sugar-free syrups like hydrogenated starch hydrolyzates, such as Lycasin, may also be replaced in part or totally by gum talha solids or syrup. The same product advantages found with hydrogenated starch hydrolyzates syrups, such as improved product shelf life, improved texture and improved aspartame stability, may also be found with the use of gum talha solids or syrup.

Recent advances use hydrogenated starch hydrolyzates (HSH) and glycerin preblended and co-evaporated to reduce moisture in some sugar-free gum formulations. Gum talha solids and/or syrup may be used to replace part or all of the HSH/glycerin blends in chewing gum formulations. Aqueous gum talha solids and/or gum talha syrup may also replace HSH in the preblend with glycerin and be co-evaporated with glycerin to obtain a low moisture, non-crystallizable blend. Combinations of gum talha solids/syrup with alditols like sorbitol, maltitol, xylitol, lactitol and mannitol in aqueous form may also be blended with glycerin and co-evaporated for use in low-moisture, sugar-free gum.

In a similar manner, gum talha solids/syrup preblended in glycerin and co-evaporated may be used in conventional sugar chewing gum formulations. Gum talha may be combined with other sugars like dextrose, sucrose, lactose, maltose, invert sugar, fructose and corn syrup solids to form a liquid mix to be blended with glycerin and co-evaporated. Gum talha solids/ syrup may also be mixed with syrup and blended with glycerin and co-evaporated for use in a sugar chewing gum formulation.

Gum talha bulking agent may also be co-dried with a variety of sugars such as sucrose, dextrose,

lactose, fructose and corn syrup solids and used in a sugar-containing gum formulation. Gum talha may be co-dried with a variety of alditols such as sorbitol, mannitol, xylitol, maltitol, palatinit and hydrogenated starch hydrolyzates and used in a sugar-free gum formulation. Co-drying refers to methods of co-crystallization and co-precipitation of gum talha with other sugars and alditols, as well as co-drying by encapsulation, agglomeration and absorption with other sugars and alditols.

These techniques include, but are not limited to, spray drying, spray chilling, fluid-bed coating and coacervation. These encapsulation techniques that give partial encapsulation or full encapsulation can be used individually or in any combination in a single step process or multiple step process. Generally, delayed release of bulk sweetener is obtained in multistep processes like spray drying the bulk sweetener and then fluid-bed coating the resultant powder.

Like gum arabic, gum talha can be used alone to encapsulate or partially encapsulate sugars and polyols, high intensity sweetners, and natural and synthetic flavors. High intensity sweetners such as aspartame, alitame, acesulfame K, salts of acesulfame, cyclamate and its salts, saccharin and its salts, sucralose, thaumatin, monellin, dihydrochalcone, stevioside, glycyrrhizin, and combinations thereof may be encapsulated in gum talha. When added to chewing gum, a fast release sweetener is obtained. Also, fast release flavors may result when encapsulated in gum talha.

The gum talha may be added to the liquid inside a liquid center gum product. The center fill of a gum product may comprise one or more carbohydrate syrups, glycerin, thickeners, flavors, acidulants, colors, sugars and sugar alcohols in conventional

amounts. The ingredients are combined in a conventional manner. The bulking agent is dissolved in the center-fill liquid and the amount of bulk sweetener added to the center-fill liquid may be about 0.1% to about 20% by weight of the entire chewing gum formula. This method of using the bulking agent in chewing gum can allow for a lower usage level of the bulking agent, can give the bulking agent a smooth release rate, and can reduce or eliminate any possible reaction of the bulking agent with gum base, flavor components or other components, yielding improved shelf stability.

Another method of using the gum talha bulking agent is to add gum talha to the dusting compound of a chewing gum. A rolling or dusting compound is applied to the surface of chewing gum as it is formed. This rolling or dusting compound serves to reduce sticking to machinery as it is formed, reduces sticking of the product to machinery as it is wrapped, and sticking to its wrapper after it is wrapped and being stored. The rolling compound comprises gum talha alone or in combination with mannitol, sorbitol, sucrose, starch, calcium carbonate, talc, other orally acceptable substances or a combination thereof. The rolling compound constitutes from about 0.25% to about 10.0%, but preferably about 1% to about 3% of weight of the chewing gum composition. The amount of gum talha added to the rolling compound is about 0.5% to 100% of the rolling compound or about 0.005% to about 5% of the chewing gum composition. This method of using gum talha in the chewing gum can allow a lower usage level of the bulking agent.

Another method of using the gum talha bulking agent is to use it in the coating/panning of a pellet chewing gum. Pellet or ball gum is prepared as conventional chewing gum, but formed into pellets that are pillow shaped or into balls. The pellets/balls can

be then sugar coated or panned by conventional panning techniques to make a sugar-coated pellet gum. The bulking agent is very stable and highly water soluble, and can be easily added to a sugar solution prepared for sugar panning.

Gum talha may be combined with sucrose, dextrose, maltose, xylitol, lactitol, palatinit, erythritol, maltitol and other new alditols in a solution to make a sugar coated pellet gum or a polyol coated pellet gum. Gum talha can also be used alone in solution in an initial gumming stage where aqueous gum talha is applied as a coating and then a powdered gum talha is added to dry the solution, as may be done in some types of "soft" panning procedures. Levels for the use of gum talha in the coating may be about 0.5 to about 20% in a sugar or polyol hard coating, or may be about 5% to 100% of dry solids in the solution or as dry powder used in the soft panning process. This process may then continue with other materials by alternating liquid and powder applications. The amount of gum talha applied may be about 0.1% to 20% of the weight of the chewing gum product, where the coating may be about 10% to 50% of the weight of the finished pellet product.

Like gum arabic, gum talha has many properties that make it an excellent coating and panning modifier. A panning modifier can improve the hardness of the coating to make it tougher, increase stickiness of coating to improve adhesion to the gum surface, especially edges, and gives additional film strength to improve shelf life of the product by protecting the gum core. Other panning modifiers which may be used in combination with gum talha are gum arabic, maltodextrin, corn syrup, corn syrup solids, gelatin, cellulose type materials like carboxymethyl

cellulose or hydroxymethyl cellulose, starch and modified starches, vegetable gums like alginates, locust bean gum, guar gum, and gum tragacanth. Other types of panning modifiers that reduce tack or act as fillers may also be used, such as insoluble carbonates like magnesium carbonate or calcium carbonate and talc. These antitack agents allow the use of a variety of carbohydrates and sugar alcohols to be used in the development of newly panned and coated gum products.

Flavors and high intensity sweeteners may also be added with the pellet coating to yield unique product characteristics. When liquid or encapsulated flavors are added to a coating, they can behave like an antitack agent. Use of gum talha can increase tackiness and help cover the flavor and allow a continuation of the sugar or polyol coating process. Also gum talha with its emulsifying properties may help bind the flavor in the coating. High intensity sweeteners can also be entrapped and stabilized in the coating with the use of gum talha. High intensity sweeteners may be applied from the dissolved coating solution, or may be applied with the powder charge addition. Sweeteners may be encapsulated and blended with the powder charge to increase stability of the high intensity sweetener.

In general, a chewing gum composition typically comprises a water-soluble bulk portion, a water-insoluble chewable gum base portion and typically water-insoluble flavoring agents. The water-soluble portion dissipates with a portion of the flavoring agent over a period of time during chewing. The gum base portion is retained in the mouth throughout the chew.

The insoluble gum base generally comprises elastomers, resins, fats and oils, waxes, softeners and inorganic fillers. Elastomers may include poly-

isobutylene, isobutylene-isoprene copolymer and styrene butadiene rubber, as well as natural latexes such as chicle. Resins include polyvinylacetate and terpene resins. Fats and oils may also be included in the gum base, including tallow, hydrogenated and partially hydrogenated vegetable oils, and cocoa butter. Commonly employed waxes include paraffin, microcrystalline and natural waxes such as beeswax and carnauba. According to the preferred embodiment of the present invention, the insoluble gum base constitutes between about 5 to about 95% by weight of the gum. More preferably the insoluble gum base comprises between 10 and 50% by weight of the gum and most preferably about 20 to about 35% by weight of the gum.

The gum base typically also includes a filler component. The filler component may be calcium carbonate, magnesium carbonate, talc, dicalcium phosphate or the like. The filler may constitute between about 5 and about 60% by weight of the gum base. Preferably, the filler comprises about 5 to about 50% by weight of the gum base.

Gum bases typically also contain softeners, including glycerol monostearate and glycerol triacetate. Further, gum bases may also contain optional ingredients such as antioxidants, colors and emulsifiers. The present invention contemplates employing any commercially acceptable gum base.

The water-soluble portion of the chewing gum may further comprise softeners, sweeteners, flavoring agents and combinations thereof. Softeners are added to the chewing gum in order to optimize the chewability and mouth feel of the gum. Softeners, also known in the art as plasticizers or plasticizing agents, generally constitute between about 0.5 to about 15.0% by weight of the chewing gum. Softeners contemplated by the present invention include glycerin, lecithin and

combinations thereof. Further, aqueous sweetener solutions such as those containing sorbitol, hydrogenated starch hydrolysates, corn syrup and combinations thereof may be used as softeners and binding agents in gum. An aqueous solution of gum talha can also be used as a softener and binding agent in gum.

As mentioned above, the gum talha bulking agent of the present invention will most likely be used in sugar gum formulations. However, sugar-free formulations are also within the scope of the invention. Sugar sweeteners generally include saccharide-containing components commonly known in the chewing gum art which comprise, but are not limited to, sucrose, dextrose, maltose, dextrin, dried invert sugar, fructose, levulose, galactose, corn syrup solids and the like, alone or in any combination.

The gum talha bulking agent of the present invention can also be used in combination with other sugarless sweeteners. Generally sugarless sweeteners include components with sweetening characteristics but which are devoid of the commonly known sugars and comprise, but are not limited to, sugar alcohols such as sorbitol, mannitol, xylitol, hydrogenated starch hydrolysates, maltitol and the like, alone or in any combination.

Depending on the particular sweetness release profile and shelf-stability needed, the gum talha bulking agent of the present invention can also be used in combination with coated or uncoated high-potency sweeteners or with high-potency sweeteners coated with other materials and by other techniques.

A flavoring agent may be present in the chewing gum in an amount within the range of from about 0.1 to about 10.0 weight percent and preferably from about 0.5 to about 3.0 weight percent of the gum. The flavoring agents may comprise essential oils, synthetic

flavors, or mixture thereof including, but not limited to, oils derived from plants and fruits such as citrus oils, fruit essences, peppermint oil, spearmint oil, clove oil, oil of wintergreen, anise, and the like. Artificial flavoring components are also contemplated for use in gums of the present invention. Those skilled in the art will recognize that natural and artificial flavoring agents may be combined in any sensorally acceptable blend. All such flavors and flavor blends are contemplated by the present invention.

Optional ingredients such as colors, emulsifiers and pharmaceutical agents may be added to the chewing gum.

In general, chewing gum is manufactured by sequentially adding the various chewing gum ingredients to a commercially available mixer known in the art. After the ingredients have been thoroughly mixed, the gum mass is discharged from the mixer and shaped into the desired form such as by rolling into sheets and cutting into sticks, extruding into chunks or casting into pellets.

Generally, the ingredients are mixed by first melting the gum base and adding it to the running mixer. The base may also be melted in the mixer itself. Color or emulsifiers may also be added at this time. A softener such as glycerin may also be added at this time, along with syrup and a portion of the bulking agent/sweetener. Further portions of the bulking agent/sweetener may then be added to the mixer. A flavoring agent is typically added with the final portion of the bulking agent. A high-intensity sweetener is preferably added after the final portion of bulking agent and flavor have been added.

The entire mixing procedure typically takes from five to fifteen minutes, but longer mixing times

may sometimes be required. Those skilled in the art will recognize that many variations of the above described procedure may be followed.

After the chewing gum center has been manufactured and shaped, as described above, the sugar or polyol coatings can be applied. Pellet or ball gum is prepared as conventional chewing gum, but formed into pellets that are pillow-shaped or ball-shaped. The pellets or balls can then be coated or panned by conventional panning techniques to make a unique, coated pellet gum. The sugar or polyols used in the coatings are very stable and highly water soluble, and can be easily added to water to make a solution prepared for panning. Sugars or polyols may be combined with other polyols or sugars, or used alone in solution as the coating on pellet gum. Sugar or polyols can also be added as a powder blended with other powders often used in some types of conventional panning procedures. Sugars or polyols can also be used with panning modifiers and other panning materials to improve product quality. Antitack agents may also be added as panning modifiers, which allow the use of a variety of carbohydrates and sugar alcohols to be used in the development of new panned or coated gum products.

The coating is initially present as a liquid syrup which contains from about 30 to about 80 or 85 weight percent of the coating ingredients previously described herein, and from about 15 to 20 to about 70 weight percent of a solvent such as water. In general, the hard coating process is carried out in a rotating pan. Sugarless gum center tablets to be coated are placed into the rotating pan to form a moving mass.

The material or syrup which will eventually form the hard coating is applied or distributed over the gum center tablets. Flavoring agents may be added

before, during and after applying the syrup to the gum centers. Once the coating has dried to form a hard surface, additional syrup additions can be made to produce a plurality of coatings or multiple layers of hard coating.

In the hard coating panning procedure, syrup is added to the gum center tablets at a temperature range of from about 100°F. to about 250°F. Preferably, the syrup temperature is from about 150°F. to about 200°F. throughout the process in order to prevent the polyol in the syrup from crystallizing. The syrup may be mixed with, sprayed upon, poured over, or added to the gum center tablets in any way known to those skilled in the art.

Each component of the coating on the gum center tablets may be applied in a single hard layer or in a plurality of hard layers. In general, a plurality of layers is obtained by applying single coats, allowing the layers to dry, and then repeating the process. The amount of solids added by each coating step depends chiefly on the concentration of the coating syrup. Any number of coats may be applied to the gum center tablet. Preferably, no more than about 75 coats are applied to the gum center tablets. More preferably, less than about 60 coats are applied and most preferably, about 30 to about 60 coats are applied. In any event, the present invention contemplates applying an amount of syrup sufficient to yield a hard coated chewing gum product containing about 10 to about 65 weight percent coating. Preferably, the final product will contain from about 20 to about 50 weight percent hard coating.

Those skilled in the art will recognize that in order to obtain a plurality of hard coated layers, a plurality of premeasured aliquots of coating syrup may be applied to the gum center tablets. It is contem-

plated, however, that the volume of aliquots of syrup applied to the gum center tablets may vary throughout the coating procedure.

The present invention contemplates that a flavoring agent may be added to the syrup, or applied to the gum center tablets while the syrup coating is drying or after the coating has dried. Furthermore, the flavoring agent may be applied anywhere within the sequence of coats, for example, after the third, twelfth, eighteenth, etc., coats.

Once a coating of syrup is applied to the gum center tablets, the present invention contemplates drying the wet syrup in an inert medium. A preferred drying medium comprises air. Preferably, forced drying air contacts the wet syrup coating in a temperature range of from about 80° to about 115°F. More preferably, the drying air is in the temperature range of from about 90° to about 105°F. The invention also contemplates that the drying air possess a relative humidity of less than about 15 percent. Preferably, the relative humidity of the drying air is less than about 8 percent.

The drying air may be passed over and admixed with the syrup coated gum centers in any way commonly known in the art. Preferably, the drying air is blown over and around the syrup coated gum center at a flow rate, for large scale operations, of about a 2800 cubic feet per minute. If lower quantities of material are being processed, or if smaller equipment is used, lower flow rates would be used. If a flavoring agent is applied after a syrup coating has been dried, the present invention contemplates drying the flavoring agent with or without the use of a drying medium.

A wide range of changes and modifications to the embodiments of the invention described above will be apparent to persons skilled in the art. For

example, while the invention is described with respect to hard-coated chewing gum, it will be appreciated that the process is applicable to coating other food products, such as candies, in which a coating with gum talha would have utility.

Examples

The following examples of the invention and comparative examples are provided by way of explanation and illustration.

The formulas listed in Table 1 comprise various sugar-type formulas in which gum talha can be added to gum after it is dissolved in water and mixed with various aqueous solvents.

TABLE 1

(WEIGHT PERCENT)

	EX. 1	EX. 2	EX. 3	EX. 4	EX. 5	EX. 6	EX. 7	EX. 8
SUGAR	55.6	56.6	55.6	47.0	53.0	53.0	55.6	47.0
BASE	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2
CORN SYRUP	12.9	1.9	8.9	2.9	6.9	6.9	0.0	2.9
PEPPER-MINT FLAVOR	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
GLY-CERIN	1.4	1.4	1.4	0.0	0.0	0.0	1.4	0.0
LIQUID/ GUM TALHA BLEND	10.0	20.0	14.0	30.0	20.0	20.0	22.9	30.0

EXAMPLE 1

Gum talha powder can be added directly to the gum.

EXAMPLE 2

A 60 gram portion of gum talha can be dissolved in 140 grams of water at 40°C making a 30% solution and added to gum.

EXAMPLE 3

Gum talha syrup at 40% solids can be added directly to the gum.

EXAMPLE 4

A blend of 60 grams of gum talha and 140 grams of water is mixed at 40°C. To this is added 100 grams of glycerin to give a mixture of 20% gum talha, 47% water, and 33% glycerin, and added to gum.

EXAMPLE 5

To 140 grams of gum talha syrup at 40% solids is added 60 grams of glycerin to give a 70% gum talha syrup with 30% glycerin, and added to gum.

EXAMPLE 6

To 140 grams of gum talha syrup of 40% solids is added 60 grams of propylene glycol giving a 70% gum talha syrup with 30% glycerin and added to gum.

EXAMPLE 7

To 140 grams of gum talha syrup at 40% solids is added 89 grams of corn syrup and blended giving a mixture of 61% gum talha syrup and 39% corn syrup.

EXAMPLE 8

To a 200 gram quantity of corn syrup is added 100 grams of glycerin. To this mixture is added 75 grams of gum talha and blended at 50°C. This mixture is added to gum.

In the next examples of sugar gum formulations, gum talha can be dissolved in water and emulsifiers can be added to the aqueous solution. Example solutions can be prepared by dissolving 15 grams of gum talha in 70 grams water and adding 15 grams of emulsifiers of various hydrophilic-lipophilic balance (HLB) values to the solution. The mixtures can then be used in the following formulas.

TABLE 2
(WEIGHT PERCENT)

	EX. 9	EX. 10	EX. 11	EX. 12	EX. 13	EX. 14
SUGAR	50.7	50.7	50.7	50.7	50.7	50.7
BASE	19.2	19.2	19.2	19.2	19.2	19.2
CORN SYRUP	12.9	12.9	12.9	12.9	12.9	12.9
GLY-CERIN	1.4	1.4	1.4	1.4	1.4	1.4
DEX-TROSE MONOHY-DRATE	9.9	9.9	9.9	9.9	9.9	9.9
PEPP. FLAVOR	0.9	0.9	0.9	0.9	0.9	0.9
BULKING AGENT EMUL-SIFIER/ WATER MIXTURE	5.0	5.0	5.0	5.0	5.0	5.0
	None	HLB=2	HLB=4	HLB=6	HLB=9	HLB=12

EXAMPLES 15-20

The same as the formulations made in Examples 9-14, respectively, except that the flavor can be mixed together with the aqueous gum talha solution and emulsified before adding the mixture to the gum batch.

The following Tables 3 through 10 are examples of gum formulations that demonstrate formula variations in which gum talha or gum talha syrup may be used.

Examples 21-24 in Table 3 demonstrates the use of gum talha in low-moisture sugar formulations showing less than 2% theoretical moisture:

TABLE 3
(WEIGHT PERCENT)

	EX. 21	EX. 22	EX. 23	EX. 24
SUGAR	57.9	53.9	48.9	25.0
GUM BASE	19.2	19.2	19.2	19.2
CORN[a] SYRUP	6.0	6.0	-	-
DEXTROSE MONOHY-DRATE	10.0	10.0	10.0	10.0
LACTOSE	0.0	0.0	0.0	5.0
GLYCERIN[b]	5.0	5.0	11.0	14.9
FLAVOR	0.9	0.9	0.9	0.9
GUM TALHA	1.0	5.0	10.0	25.0

[a]Corn Syrup is evaporated to 85% solids, 15% moisture

[b]Glycerin and syrup may be blended and co-evaporated

Examples 25-28 in Table 4 demonstrate the use of gum talha in medium-moisture sugar formulations having about 2% to about 5% moisture.

Examples 29-32 in Table 5 demonstrate the use of gum talha in high-moisture sugar formulations having more than about 5% moisture.

TABLE 4
(WEIGHT PERCENT)

	EX. 25	EX. 26	EX. 27	EX. 28
SUGAR	52.5	48.5	43.5	25.0
GUM BASE	19.2	19.2	19.2	19.2
CORN SYRUP[a]	15.0	15.0	13.0	12.5
DEXTROSE MONOHY-DRATE	10.0	10.0	10.0	10.0
GLYCERIN[b]	1.4	1.4	3.4	7.4
FLAVOR	0.9	0.9	0.9	0.9
GUM TALHA	1.0	5.0	10.0	25.0

[a]Corn Syrup is evaporated to 85% solids, 15% moisture

[b]Glycerin and syrup may be blended and co-evaporated

TABLE 5
(WEIGHT PERCENT)

	EX. 29	EX. 30	EX. 31	EX. 32
SUGAR	50.0	46.0	41.0	25.0
GUM BASE	24.0	24.0	24.0	24.0
CORN SYRUP	24.0	24.0	24.0	24.6
GLYCERIN	0.0	0.0	0.0	0.4
FLAVOR	1.0	1.0	1.0	1.0
GUM TALHA	1.0	5.0	10.0	25.0

Examples 33-36 in Table 6 and Examples 37-44 in Tables 7 and 8 demonstrate the use of gum talha in low- and high-moisture gums that are sugar-free. Low-moisture gums have less than about 2% moisture, and high-moisture gums have greater than 2% moisture.

TABLE 6
(WEIGHT PERCENT)

	EX. 33	EX. 34	EX. 35	EX. 36
BASE	25.5	25.5	25.5	25.5
SORBITOL	50.0	46.0	41.0	21.0
MANNITOL	12.0	12.0	12.0	12.0
GLYCERIN	10.0	10.0	10.0	15.0
FLAVOR	1.5	1.5	1.5	1.5
GUM TALHA	1.0	5.0	10.0	25.0

TABLE 7
(WEIGHT PERCENT)

	EX. 37	EX. 38	EX. 39	EX. 40
BASE	25.5	25.5	25.5	25.5
SORBITOL	50.0	46.0	31.0	6.0
LIQUID SORBITOL*	10.0	10.0	20.0	30.0
MANNITOL	10.0	10.0	10.0	10.0
GLYCERIN	2.0	2.0	2.0	2.0
FLAVOR	1.5	1.5	1.5	1.5
GUM TALHA	1.0	5.0	10.0	25.0

*Sorbitol Liquid contains 70% sorbitol, 30% water

TABLE 8
(WEIGHT PERCENT)

	EX. 41	EX. 42	EX. 43	EX. 44
BASE	25.5	25.5	25.5	25.5
SORBITOL	50.0	44.0	35.0	15.0
HSH SYRUP*	10.0	10.0	10.0	10.0
MANNITOL	8.0	8.0	8.0	8.0
GLYCERIN**	4.0	6.0	10.0	15.0
FLAVOR	1.5	1.5	1.5	1.5
GUM TALHA	1.0	5.0	10.0	25.0

* Hydrogenated starch hydrolyzate syrup
** Glycerin and HSH syrup may be blended or co-evaporated

Table 9 shows sugar chewing formulations that can be made with various other types of sugars.

TABLE 9
(WEIGHT PERCENT)

	EX. 45	EX. 46	EX. 47	EX. 48	EX. 49	EX. 50
GUM BASE	19.2	19.2	19.2	19.2	19.2	19.2
SUCROSE	44.5	24.5	39.5	19.5	29.5	19.5
GLYCERIN	1.4	6.4	1.4	6.4	1.4	6.4
CORN SYRUP	14.0	14.0	14.0	14.0	14.0	14.0
DEXTROSE	5.0	5.0	-	-	10.0	5.0
LACTOSE	5.0	5.0	10.0	10.0	-	-
FRUCTOSE	5.0	5.0	10.0	10.0	10.0	5.0
INVERT SUGAR	-	-	-	-	10.0	10.0
MALTOSE	-	-	-	-	-	-
CORN SYRUP SOLIDS	-	-	-	-	-	-
PEPPERMINT FLAVOR	0.9	0.9	0.9	0.9	0.9	0.9
GUM TALHA	5.0	20.0	5.0	20.0	5.0	20.0

	EX. 51	EX. 52	EX. 53	EX. 54	EX. 55	EX. 56
GUM BASE	19.2	19.2	19.2	19.2	19.2	19.2
SUCROSE	29.5	19.5	29.5	19.5	37.5	22.5
GLYCERIN	1.4	6.4	1.4	6.4	1.4	6.4
CORN SYRUP	14.0	14.0	14.0	14.0	11.0	11.0
DEXTROSE	10.0	5.0	10.0	5.0	10.0	5.0
LACTOSE	-	-	-	-	-	-
FRUCTOSE	10.0	5.0	10.0	5.0	5.0	5.0
INVERT SUGAR	10.0	10.0	-	-	5.0	5.0
MALTOSE	-	-	10.0	10.0	-	-
CORN SYRUP SOLIDS	-	-	-	-	5.0	5.0
PEPPERMINT FLAVOR	0.9	0.9	0.9	0.9	0.9	0.9
GUM TALHA	5.0	20.0	5.0	20.0	5.0	20.0

Table 10 shows chewing gum formulations that are free of sugar. These formulations can use a wide variety of other non-sugar alditols.

TABLE 10
(WEIGHT PERCENT)

	EX. 57	EX. 58	EX. 59	EX. 60	EX. 61	EX. 62
GUM BASE	25.5	25.5	25.5	25.5	25.5	25.5
GLYCERIN	8.0	8.0	8.0	8.0	8.0	2.0
SORBITOL	38.0	28.0	28.0	23.0	22.0	10.0
MANNITOL	-	10.0	10.0	10.0	10.0	6.0
SORBITOL LIQUID	17.0	17.0	-	-	-	-
LYCASIN	-	-	17.0	12.0	8.0	20.0
MALTITOL	-	-	-	10.0	-	-
XYLITOL	-	-	-	-	15.0	15.0
LACTITOL	-	-	-	-	-	-
PALATINIT	-	-	-	-	-	-
FLAVOR	1.5	1.5	1.5	1.5	1.5	1.5
GUM TALHA	10.0	10.0	10.0	10.0	10.0	20.0

TABLE 10 (Cont'd)
(WEIGHT PERCENT)

	EX. 63	EX. 64	EX. 65	EX. 66	EX. 67	EX. 68
GUM BASE	25.5	25.5	25.5	25.5	25.5	25.5
GLYCERIN	8.0	8.0	8.0	2.0	8.0	2.0
SORBITOL	32.0	27.0	22.0	31.0	10.0	10.0
MANNITOL	8.0	8.0	8.0	-	-	-
SORBITOL LIQUID	5.0	-	-	-	-	-
LYCASIN	-	5.0	5.0	5.0	10.0	20.0
MALTITOL	-	5.0	-	-	-	-
XYLITOL	-	-	-	15.0	15.0	-
LACTITOL	10.0	10.0	10.0	-	-	-
PALATINIT	-	-	10.0	10.0	10.0	21.0
FLAVOR	1.5	1.5	1.5	1.5	1.5	1.5
GUM TALHA	10.0	10.0	10.0	10.0	20.0	20.0

High-intensity sweeteners such as aspartame, acesulfame K, or the salts of acesulfame, cyclamate and its salts, saccharin and its salts, alitame, sucralose, thaumatin, monellin, dihydrochalcone, stevioside, glycyrrhizin, and combinations thereof may be used in any of the Examples listed in Tables 3, 4, 5, 6, 7, 8, 9 and 10. Since gum talha has less sweetness than some of the other sugars used in sugar gum, and some of the alditols in sugar-free gum, a high-intensity sweetener may be need to obtain the proper level of sweetness.

High-intensity sweeteners may also be modified to control their release in chewing gum formulations containing gum talha. This can be controlled by various methods of encapsulation, agglomeration, absorption, or a combination of methods to obtain either a fast or slow release of the sweetener. Sweetener combinations, some of which may be synergistic, may also be included in the gum formulations containing gum talha.

The following examples show the use of high-intensity sweeteners in chewing gum formulations with gum talha.

EXAMPLE 69

Aspartame at a level of 0.2% may be added to any of the formulas in Tables 3 through 10 by replacing 0.2% of the gum talha.

EXAMPLE 70

Alitame at a level of 0.03% may be added to any of the formulas in Tables 3 through 10 by replacing 0.03% of the gum talha.

EXAMPLE 71

Sucralose at a level of 0.07% may be added to any of the formulas in Tables 3 through 10 by replacing 0.07% of the gum talha.

EXAMPLE 72

Thaumatin at a level of 0.02% may be added to any of the formulas in Tables 3 through 10 by replacing 0.02% of the gum talha.

EXAMPLE 73

Glycyrrhizin at a level of 0.4% may be added to any of the formulas in Tables 3 through 10 by replacing 0.4% of the gum talha.

High-intensity sweeteners may also be combined with other high-intensity sweeteners, with or without encapsulation, agglomeration or absorption, and used in chewing gum. Examples are:

EXAMPLE 44

Aspartame and acesulfame K at a 1:1 ratio may be added to any of the formulas in Tables 3 through 10 at a level of 0.15% by replacing 0.15% of the gum talha.

EXAMPLE 75

Aspartame and alitame at a ratio of 9:1 aspartame: alitame may be added to any of the formulas in Tables 3 through 10 at a level of 0.1% by replacing 0.1% of the gum talha.

EXAMPLE 76

Aspartame and thaumatin at a ratio of 9:1 aspartame:thaumatin can be added to any of the formulas in Tables 3 through 10 at a level of 0.1% by replacing 0.1% of the gum talha.

EXAMPLE 77

Sucralose and alitame in a ratio of 3:1 sucralose: alitame can be added to any of the formulas in Tables 3 through 10 at a level of 0.5% by replacing 0.5% of the gum talha.

EXAMPLE 78

Alitame and glycyrrhizin in a ratio of 1:12 alitame:glycyrrhizin can be added to any of the

formulas in Tables 3 through 10 at a level of 0.1% by replacing 0.1% of the gum talha.

EXAMPLE 79

Aspartame and glycyrrhizin in a ratio of 1:14 aspartame:glycyrrhizin can be added to any of the formulas in Tables 3 through 10 at a level of 0.3% by replacing 0.3% of the gum talha.

As noted earlier, the gum formulas can be prepared as stick or tab products in the sugar or sugarless type formulations. These formulas can also be made in a pellet or pillow shape pellet or a round ball or any other shape of product for coating/panning. However, gum formulas are generally adjusted to a higher level of gum base to give a more consumer acceptable size of gum bolus.

Keeping this in mind, if a coating of about 25% of the total product is added to a pellet core as sugar or polyols, the gum base in the pellet core should also be increased by 25%. Likewise, if a 33% coating is applied, the base levels should also be increased by 33%. As a result, gum centers are usually formulated with about 25% to about 40% gum base with a corresponding decrease in the other ingredients except flavor. Generally flavors increase with the level of gum base as the base tends to bind flavors into the gum and more flavor is needed to give a good flavorful product. However flavors can also be added to the coating to give increased flavor impact and more flavor perception.

Some typical sugar type gum center formulations are shown in Table 11.

TABLE 11
(WEIGHT PERCENT)

	EX. 80	EX. 81	EX. 82	EX. 83	EX. 84	EX. 85
SUGAR	52.0	49.0	48.0	44.0	41.0	39.0
GUM BASE	26.0	30.0	35.0	26.0	30.0	35.0
CORN SYRUP	20.0	19.0	15.0	18.0	17.0	14.0
GLYCERIN	1.0	1.0	1.0	1.0	1.0	1.0
PEPPERMINT FLAVOR	1.0	1.0	1.0	1.0	1.0	1.0
DEXTROSE MONOHYDRATE	-	-	-	10.0	10.0	10.0

Formulations can also be made similar to those found in Tables 1-5 for low, medium, and high moisture formulas. Higher levels of base may be used with a corresponding decrease in other ingredients. Also, other sugars may be used in the gum center as found in Table 9.

Gum talha can then be used in the coating formula on the various pellet gum formulations. The following Table 12 shows some sugar and dextrose type formulas:

TABLE 12
(DRY WEIGHT PERCENT)

	EX. 86	EX. 87	EX. 88	EX. 89	EX. 90	EX. 91
SUGAR	97.1	95.4	94.1	96.9	95.1	93.6
GUM TALHA	2.0	3.0	4.0	2.0	3.0	4.0
TITANIUM DIOXIDE	0.5	1.0	1.0	-	-	-
CALCIUM CARBONATE	-	-	-	0.5	1.0	2.0
FLAVOR	0.3	0.5	0.8	0.5	0.8	0.3
WAX	0.1	0.1	0.1	0.1	0.1	0.1

	EX. 92	EX. 93	EX. 94	EX. 95
DEXTROSE MONOHYDRATE	97.6	95.4	97.2	94.5
GUM TALHA	1.5	3.0	1.5	3.0
TITANIUM DIOXIDE	0.5	1.0	-	-
CALCIUM CARBONATE	-	-	1.0	2.0
FLAVOR	0.3	0.5	0.2	0.4
WAX	0.1	0.1	0.1	0.1

The above formulations are made by making a syrup by dissolving the sugar and gum talha in solution at about 75% solids at boiling, and suspending titanium dioxide or calcium carbonate in this syrup. Flavor is not mixed with the hot syrup, but added at low levels with one or more coats. After the final coats are applied and dried, wax is applied to give a smooth polish.

The above process gives a hard shell coating. Often a dry charge of powdered sugar or dextrose monohydrate may be used. This gives a somewhat softer coating. A dry charge may be used to build up a coating, but then finished with a straight syrup to obtain a hard shell. Table 13 gives these types of formulas.

TABLE 13
(DRY WEIGHT PERCENT)

	EX. 96	EX. 97	EX. 98	EX. 99	EX. 100	EX. 101
SUGAR	77.5	81.4	-	-	87.5	-
DEXTROSE MONOHYDRATE	-	-	77.5	86.3	-	87.1
POWDER SUGAR*	20.0	15.0	-	-	-	-
POWDER DEXTROSE*	-	-	20.0	10.0	-	-
GUM TALHA POWDER	2.0	3.0	2.0	3.0	8.0	8.0
GUM TALHA SOLUTION	-	-	-	-	4.0	4.0
FLAVOR	0.4	0.5	0.4	0.6	0.4	0.8
WAX	0.1	0.1	0.1	0.1	0.1	0.1

* Powder and/or crystalline sugar may be used.

In Examples 96-99, gum talha is blended in the sugar syrup. In Examples 100 and 101, gum talha powder is dry charged after a gum talha solution is applied in the first stages of coating, then this is followed by a hard shell coating of sugar solution or dextrose solution.

Gum talha may also be used in coating of sugarless gum centers. Like sugar gum centers, the base formulation can be increased in proportion to the amount of coating applied to the center. Formulations similar to those found in Tables 6, 7 or 8 for low and high moisture gum can be used to make gum centers. Generally, the base level may be increased to 30-46% with the other ingredients proportionally reduced. Some typical gum formulas are in Table 14.

TABLE 14
(WEIGHT PERCENT)

	EX. 102	EX. 103	EX. 104	EX. 105	EX. 106	EX. 107	EX. 108
GUM BASE	35.0	35.0	30.0	30.0	30.0	40.0	30.0
CALCIUM CARBONATE	-	-	5.0	10.0	15.0	-	-
SORBITOL	43.3	45.3	46.3	40.3	44.8	41.7	46.5
MANNITOL	10.0	10.0	5.0	10.0	-	8.0	10.0
GLYCERIN	-	8.0	2.0	-	8.0	2.0	2.0
SORBITOL LIQUID	10.0	-	10.0	8.0	-	6.0[a]	10.0[a]
FLAVOR	1.5	1.5	1.5	1.5	2.0	2.0	1.3
HIGH INTENSITY SWEETENER	0.2	0.2	0.2	0.2	0.2	0.3	0.2

a) Lycasin brand hydrogenated starch hydrolyzate used instead of sorbitol liquid

In the above center formulations, the high intensity sweetener used is aspartame. However other high intensity such as alitame, acesulfame K, salts of acesulfame, cyclamate and its salts, saccharin and its salts, sucralose, thaumatin, monellin, dihydrochalcone, stevioside, glycyrrhizin and combinations thereof may be used in any of the examples with the level adjusted for sweetness.

Lycasin and other polyols such as maltitol, xylitol, lactitol, palatinit (isomalt) may also be used in the gum center formulations at various levels similar to those shown in Table 10. The texture may be adjusted by varying glycerin or sorbitol liquid. Sweetness of the center formulation can also be adjusted by varying the level of high intensity sweetener.

Gum talha is especially useful in sugarless coatings with xylitol, sorbitol, maltitol, lactitol, isomalt (hydrogenated isomaltolose) and erythritol.

Gum talha acts as a binder, film former, hardener of the coated pellet. The following table gives formulas for a xylitol coating:

TABLE 15
(DRY WEIGHT PERCENT)

	EX. 109	EX. 110	EX. 111	EX. 112	EX. 113	EX. 114
XYLITOL	94.8	92.4	90.7	90.1	89.9	88.8
GUM TALHA	4.0	6.0	7.0	8.5	8.5	10.0
FLAVOR	0.5	0.5	0.7	0.7	0.9	0.5
TITANIUM DIOXIDE	0.5	0.9	-	0.5	0.5**	0.5**
TALC	0.1	0.1	0.1	0.1	0.1	0.1
WAX	0.1	0.1	0.1	0.1	0.1	0.1
COLOR*	-	-	1.4	-	-	-

* Lake color dispersed in xylitol solution
** Calcium carbonate used in place of titanium dioxide

The above formulas are used to coat pellets by applying a xylitol/gum talha solution in multiple coats and air drying. Color or whitener is also mixed in the solution. After pellets have been coated and dried, talc and wax are added to give a polish.

Like xylitol, erythritol coating also requires a binder, film former, and hardener in the coating to make an acceptable product. The following formulations can be made:

TABLE 16
(DRY WEIGHT PERCENT)

	EX. 115	EX. 116	EX. 117	EX. 118	EX. 119	EX. 120
ERYTHRITOL	93.8	91.5	89.2	90.1	88.4	86.8
GUM TALHA	5.0	7.0	8.5	8.5	10.0	12.0
FLAVOR	0.5	0.4	0.7	0.7	0.9	0.5
TITANIUM DIOXIDE	0.5	0.9	-	0.5	0.5	0.5
TALC	0.1	0.1	0.1	0.1	0.1	0.1
WAX	0.1	0.1	0.1	0.1	0.1	0.1
COLOR	-	-	1.4*	-	-	-

* Lake color dispersed in erythritol solution

The above formulas are used to coat pellets by applying a erythritol/gum talha solution in multiple coats and air drying. Color or whitener is also mixed in the solution. After pellets have been coated and dried, talc and wax are added to give a polish.

For coating formulas based on sorbitol, maltitol, lactitol, and isomalt, gum talha can be used as a binder and film former, and a crystallization modifier to help facilitate coating. Generally these polyols are more difficult to coat using only a straight syrup, but with proper technique a good smooth hard shell can be made. However, it may be preferable to add a dry charge to quicken the drying process before the pellets get too sticky. The following formulations may be used.

TABLE 17
(DRY WEIGHT PERCENT)

	EX. 121	EX. 122	EX. 123	EX. 124	EX. 125	EX. 126
SORBITOL	96.8	94.9	92.1	86.8	76.1	69.5
SORBITOL POWDER	-	-	-	10.0	20.0	25.0
GUM TALHA	2.0	4.0	6.0	2.0	3.0	4.0
FLAVOR	0.5	0.4	0.7	0.5	0.3	0.7
TITANIUM DIOXIDE	0.5	0.5	1.0	0.5	0.4	0.6
TALC	0.1	0.1	0.1	0.1	0.1	0.1
WAX	0.1	0.1	0.1	0.1	0.1	0.1

Sorbitol powder is used to dry charge in the early stages of coating. Sorbitol, gum talha, and whitener is blended into a syrup and applied to pellets. After all coating is applied and dried, talc and wax are added to give a polish.

In a similar manner, coatings with maltitol, lactitol, and isomalt may be made in the coating formulas in Table 17 by replacing sorbitol with any one of the other polyols and sorbitol powder with the polyol powder. Like sorbitol, the other polyols may become sticky during the coating and drying process, so the dry powder charge may be needed to give the proper drying. In the later stages of the coating process less gum talha could be used and a more pure polyol syrup could be used to give a smooth surface. Also, the dry charge would only be used in the early stages of the coating process.

In addition to dry charging with the specific polyol, other ingredients may be added to the dry charge to help absorb moisture. These materials could be inert such as talc, calcium carbonate, magnesium carbonate, starches, gums like gum talha or other moisture absorbing materials. Also, powdered

sweeteners or flavors could be added with the dry charge.

Some polyols such as sorbitol, maltitol, lactitol, or isomalt are not sufficiently sweet compared to sugar or xylitol, so high intensity sweeteners may be added to the coating such as aspartame, acesulfame K, salts of acesulfame, cyclamate and its salts, saccharin and its salts, alitame, sucralose, thaumatin, monellin, dihydrochalcone, glycyrrhizin, and combinations thereof. If a hot syrup is applied, heat may degrade the sweetener so only stable sweeteners should be used. Generally high intensity sweeteners are added with the polyol/gum talha solution to obtain an even distribution in the coatings.

Liquid flavors generally are not added throughout the coating but at specific points throughout the process. When flavor is added, less air is used for drying until the flavor coating is covered by the next coatings and dried. Flavors may be various spearmint, peppermint, wintergreen, cinnamon, and fruit flavors to yield a wide variety of flavored chewing gum products.

It should be appreciated that the compositions and methods of the present invention are capable of being incorporated in the form of a variety of embodiments, only a few of which have been illustrated and described above. The invention may be embodied in other forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive, and the scope of the invention, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of

equivalency of the claims are to be embraced within their scope.

I CLAIM:

1. A chewing gum composition comprising:

a) about 5% to about 95% gum base;

b) about 0.1% to about 10% of a flavoring agent, and

c) about 5% to about 95% bulking and sweetening agents, the bulking and sweetening agents comprising gum talha.

2. The chewing gum composition of claim 1 wherein the gum talha is in the form selected from the group consisting of powder gum talha, gum talha syrup and mixtures thereof.

3. A chewing gum product including gum talha wherein the gum talha is used as a dusting agent on the surface of the gum.

4. A coated chewing gum product comprising a gum pellet coated with a hard coating, the hard coating comprising gum talha.

5. The method of Claim 4 wherein the gum talha comprises 0.5 to 20% of the hard coating

6. The method of Claim 4 wherein the hard coating further comprises a polyol selected from the group consisting of xylitol, lactitol, maltitol, hydrogenated isomatolose, erythritol and mixtures thereof

7. The method of Claim 4 wherein the hard coating further comprises a flavor.

8. The method of Claim 4 wherein the hard coating further comprises a high potency sweetener.

9. The method of Claim 4 wherein the hard coating further comprises a sugar selected from the group consisting of sucrose, dextrose, maltose and mixtures thereof.

10. The method of Claim 4 wherein the hard coating further comprises a coating modifier.

11. A method of making chewing gum comprising the steps of:

a) coevaporating an aqueous solution comprising gum talha and a plasticizing agent to form a syrup, and

b) mixing the syrup with gum base, bulking agents and flavoring agents to produce a gum composition.

12. A chewing gum composition sweetened at least in part by aspartame, the gum composition containing an effective amount of gum talha to stabilize the aspartame against degradation into non-sweetening derivatives.

13. A method of making chewing gum comprising the steps of:

a) codrying a solution containing gum talha and a sweetener selected from the group consisting of sugar sweeteners, alditol sweeteners and high-potency sweeteners, and

b) mixing the codried gum talha/ sweetener with gum base and flavoring agents to produce a gum composition.

14. A liquid filled chewing gum product wherein the liquid fill comprises gum talha.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A23G 3/30
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B. FIELDS SEARCHED

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, JPO
search term: chewing gum, talha

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,576,663 (SIGNORINO ET AL) 27 April 1971.	1-14
A	US, A, 4,317,838 (CHERUKURI ET AL) 02 March 1982.	1-14
A	US, A, 5,084,298 (HUSSEIN ETAL) 28 January 1992.	1-14
A	US, A, 5,135,761 (DAVE ETAL) 04 August 1992.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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(54) Title: SINTERED, SOLID PIECE, WATER SOLUBLE OR DISPERSIBLE BEVERAGE COMPOSITION AND METHOD FOR ITS PREPARATION

(57) Abstract: Sintered beverage compositions in solid piece form which disperse and dissolve rapidly upon contact with water. Method for producing solid piece, water soluble or water dispersible beverage compositions. Said composition comprise dry particulates bound by a finely dispersed glassy phase, which comprises 10 40 wt % of the composition.

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SINTERED, SOLID PIECE, WATER SOLUBLE OR DISPERSIBLE BEVERAGE COMPOSITION AND METHOD FOR ITS PREPARATION

Field of the invention

The invention relates to beverage compositions, in particular to beverage compositions which disperse and dissolve rapidly upon contact with water.

Background of the invention

Solid beverage compositions that dissolve in water to produce the desired beverage are known and are commonly produced in powder, granule or tablet form. Such beverage compositions include instant coffee, tea, iced tea, chocolate (e.g. Milo®), soups and sport nutrition drinks, such as the PowerBar® beverage system.

Powder compositions are often hygroscopic and so caking of the powder is a problem. Anti-caking agents may be added to overcome this problem but these can impair the taste and appearance of the resulting beverage and increase the cost. Further problems associated with powdered beverage compositions are dust and lack of convenience in making up the drink, such as the need to measure the required dose of powder and the risk of spillage.

Various sports nutrition drinks come in powder form and are sold in large tubs with a small scoop to measure out the correct amount to make up with water. They are also sold in convenient single serve sachets of the exact amount to be made up in a standard volume, often a 500 ml bottle. An example of such products are PowerBar® Endurance Sport Drink powder mix (Powerbar Inc.), Gatorade ® Stix (PepsiCo, Inc.) and Isostar ® energy drink powder (Nutrition et Santé SAS). Ease of measuring a dose and minimising risk of spillage are particularly important for such products since they are primarily used by athletes who want to make up the drink in a water bottle whilst on the move. These products at best allow pouring of the required dose into a water bottle, but this is difficult whilst on the move without some of the material spilling or blowing away.

Pressed tablets provide a convenient dosage form but even with the inclusion of disintegrants in the composition such products do not dissolve rapidly. US 2003/0026836 relates to powders and tablets based on a carbohydrate matrix with improved dissolution properties in water. The components of the powder or tablet are subjected to treatment with a gas so that gas is entrapped therein and sufficient closed porosity is provided so that the entrapped gas promotes dissolution or dispersion upon contact with water. The need to incorporate gas into the components of the pressed tablet adds cost and complexity to the manufacturing process.

US 4,031,238 relates to dry water-soluble beverage cubes containing powdered crystalline glucose monohydrate, crystalline sucrose and a hygroscopic flavour material. The cubes are prepared by heating the mixed ingredients to above 95 °F (35 °C) in a high humidity atmosphere to solidify the mass. Under these conditions the hygroscopic flavour material absorbs moisture and these articles then wet adjacent sugar particles causing partial or complete dissolution of them. In effect, the flavour material acts as a binding agent for the system.

Rapid dissolution without the problems associated with tablets and powders may be achieved by sintering a powder to produce a granular beverage material. EP 0 373 697 describes such a method which comprises sintering an essentially dry powdered beverage extract by heating the extract in a closed environment to form an agglomerate in which the particles of the powder have been brought in a point-to-point contact so that they are bridged to one another without loosing their identity, and then granulating the agglomerate. However a problem with such a product is lack of convenience in making up the drink, particularly in the case of an athlete on the move as described above.

An object of the invention is to provide a beverage composition in solid piece-form which disperses and dissolves rapidly upon addition to water, and a method for making such a composition.

Summary of the invention

In a first aspect the invention relates to a sintered, solid piece, water soluble or water dispersible beverage composition comprising dry particulates bound by a finely dispersed glassy phase which constitutes 10 to 40 wt % of the composition. The finely dispersed glassy phase acts as a bonding agent to link components that would otherwise not be prone to join to each other under moderate conditions. Such a composition is easy to handle. Further, the composition has high open porosity and readily solvated (by water) inter-particle bonding which allows rapid ingress of water into the depth of the composition. Consequently, upon contact with water, the composition rapidly disintegrates and the particles disperse and are free to dissolve.

In a second aspect the invention relates to a method for producing a solid piece, water soluble or water dispersible beverage composition comprising:

(a) providing a powder comprising 10 to 40 wt % glassy phase particles and 60 to 90 wt % one or more other dry particulate components; and

(b) sintering the powder, such that the glassy phase particles melt at their surface and wet and bond neighbouring particles to form a structured, porous, fused product.

During the sintering treatment, the finely dispersed glassy phase particles acquire sufficient mobility to wet and bond neighbouring particles in contact and so achieve a 3-dimensional network structure through the whole mass. The resulting composition has high open porosity and readily solvated (by water) inter-particle bonding which allows rapid ingress of water into the depth of the body. Consequently, upon contact with water, the body rapidly disintegrates and the particles disperse and are free to dissolve.

Detailed description of the invention

In one aspect the invention relates to a sintered, solid piece, water soluble or water dispersible beverage composition comprising dry particulates bound by a finely dispersed glassy phase which comprises 10 to 40 wt % of the composition.

"Beverage composition" is any composition that can be dissolved or dispersed in water to produce a beverage, such as coffee, tea, iced tea, chocolate, soup and sport nutrition drinks.

"Solid piece" means that the beverage composition consists of a mass, or coherent body, of substance as opposed to a powder or granules. The mass is preferably porous and of a size which is easy to handle and suitable for adding to a cup, glass or bottle of water.

"Sintering" is a method for forming such a coherent mass by heating and is a method for making objects from powder, increasing the adhesion between particles as they are heated. The particles of the starting material are only brought in a kind of point-to-point contact in which the particles are "bridged" to one another without losing their identity as a particle. According to the invention the glassy material acts as the bridging agent. During the sintering process the glassy phase particles become viscous and wet and bond neighbouring particles to form a structured, porous, fused product.

"Glassy phase" means an amorphous (or glassy) solid, rather than a crystalline solid.

The beverage composition comprises dry particulates which are selected according to the desired resulting beverage. Particulates having a diameter of 10 to 100 μm are preferred since extremely large particulates are too slow to dissolve and a very small particle size would mean there were not enough glassy particles to form the links. The dry particulates may include, but are not limited to, one or more of crystalline sugars, maltodextrin, protein powders, cereal components, fruit powders, powdered gum, cocoa, coffee powder, tea powder, herbs, and heat sensitive ingredients such as volatile flavour ingredients, heat sensitive vitamins and nutritional powders, such as fruit or milk. Further, particles with a fragile structure and/or low density may be incorporated intact. These may be such that they hydrate and float to the surface of the beverage after dispersion. Examples of such materials are freeze-dried fruit, dried marshmallow shapes, dried pasta shapes or croutons. Such low-density materials could not be formed into a beverage tablet by tablet-pressing as their structure would be destroyed. The dry

particulates comprise 60 to 90 wt % of the weight of the composition, preferably 75 to 85 wt %.

The dry particulates are bound by a finely dispersed glassy phase. Sugar glasses stable over time are conventionally manufactured from mixtures of carbohydrates. The glassy bonding phase can be made up from a wide variety of carbohydrate materials encompassing both sugar and sugar-free ingredient types. In particular the glassy bonding phase may preferably comprise corn syrup solids or dextrins or two or more of sucrose, dextrose, fructose, maltose, lactose, corn syrup solids, dextrins, sorbitol, isomalt, maltitol, xylitol, erythritol and polydextrose.

The glassy material comprises 10 to 40 wt % of the weight of the composition, preferably 15 to 25 wt %. Since only a minor proportion of glassy bonding material is required in order to link the other components, the other components can be selected for other qualities, e.g. nutritional value, flavour, structure, etc.

The glassy material is milled to a fine powder, preferably with the median particle size (d50) smaller than 10 μm, such that in the resulting beverage composition the material is finely dispersed. The glassy material acts as a binding agent in the beverage composition and acts to bond neighbouring particles in contact and so achieve a 3-dimensional network structure through the whole mass. Alternatively, the glassy material may act as a binding agent at the outer surface of the solid piece beverage composition only, leaving the inner dry particulate contents unbound. This allows even more rapid dispersal and dissolution of the particles upon contact with water.

The sintered, solid piece, water soluble or water dispersible beverage composition of the invention preferably has a density of 0.5 to 1.0 g/cm^3, most preferably about 0.7 g/cm^3. The sintered, solid piece, water soluble or water dispersible beverage composition of the invention preferably has a porosity of 35 % and 70 %, most preferably about 55 %. This allows water percolation into the structure thus improving dispersion and dissolution of the composition upon contact with water.

The composition disperses rapidly upon contact with water and then rapidly dissolves with agitation. Preferably the sintered solid piece disintegrates in less than 10 seconds for 50 g of sample of any dimensions in 500 ml of water at 15 °C. However, the dispersion rate of these compositions depends on the dimensions of the solid piece rather than simply on the mass. For example, a 10 mm diameter rod would disperse at much the same speed whatever its length (and therefore its weight) providing there was sufficient water.

Preferably the solid piece composition is a dose-sized portion.

The composition has many uses including:

- A sport nutrition drink for use by athletes who wish to make up the drink quickly and easily whilst on the move. The composition may be produced in a stick-shaped, dose-sized portion suitable for a standard size water bottle (e.g. 500 ml), which can then be passed through the neck of such a water bottle to dissolve quickly and easily.
- A composition to be added to hot water to produce a hot drink, such as tea, coffee, chocolate, soup. The solid portion is simply dropped into hot water, in which it disperses and dissolves rapidly to produce the drink. No measuring is required and there is no risk of powder spillage or dust.
- A composition to be added to cold water to produce a beverage such as iced tea or a milk drink. The solid portion is simply dropped into cold water, in which it disperses and dissolves rapidly to produce the drink. No measuring is required and there is no risk of powder spillage or dust.
- A composition to be added to cold water to produce a beverage containing heat sensitive ingredients such as volatile flavour ingredients, heat sensitive vitamins and nutritional powders, such as fruit or milk.
- A composition to be added to water to produce a beverage with inclusions of fragile low density materials which float to the top of the drink.

In a further aspect the invention provides a method for producing a solid piece beverage composition comprising:

(a) providing a powder comprising 10 to 40 wt % glassy phase particles and 60 to 90% one or more other dry particulate components; and

(b) sintering the powder, such that the glassy phase particles melt at their surface and wet and bond neighbouring particles to form a structured, porous, fused product.

According to one aspect, the glassy phase particles as described above have been milled to a fine powder prior to mixing with the dry particulate component(s) as described above. Preferably the glassy phase particles are milled to a fine powder with the median particle size (d50) smaller than 10 μm prior to intimate mixing with one or more other dry particulate components.

According to another aspect, the glassy phase particles may be co-milled together with the other dry particulate components.

The glassy phase particles comprise 10 to 40 wt % of the beverage composition, preferably 15 to 25 wt %.

The resulting mixture in both cases has a low bulk density of around 0.5 g/cm^3.

A mould is filled with this mixture, optionally with some degree of tamping to assure a degree of close-packing of the particles (particle-particle contact). The mould should represent the desired finished shape of the product, e.g. a simple capped cylindrical tube. Further, the mould may also provide the packaging for the product. However, the mould need not have such dual purpose and in principle could be from any suitable food grade material, such as a semi-rigid polymer. The solid piece beverage composition will closely follow the shape of the mould faces with which it has initial contact. Hence, the mould may be of a form with specific shape interest or functionality and may carry quite detailed figuring or engraving of design or lettering which will be transferred onto the surface of the solid piece.

The mixture contained in the mould is then subjected to a sintering heat treatment. Preferably the mould is sealed closed during the treatment. Hermetic closure is useful to prevent moisture loss on heating which might inhibit the sintering process. Alternatively, sintering may be carried out in an atmosphere with a controlled relative

humidity to provide greater process control and flexibility. The mould preferably stays in the same orientation during the heat treatment.

The time and temperature of heat treatment is partially determined by the composition of the glassy phase. Temperature should be in the vicinity of the onset of mobility at the glass transition. With progressive increase of temperature above the glass transition temperature (Tg), mobility of the glassy phase particles rises dramatically. Hence, at higher temperature the required residence time should be shorter. However, with a body of substantial size, the inevitable temperature gradient during heating can cause an unwanted inhomogeneity of sintering through the piece. For this reason relatively long duration treatment at modest temperature is favoured. For most formulations treatment will be at 50 to 60 °C for 5 to 10 hours. Such a low temperature heat treatment allows the use of heat-sensitive ingredients and allows the incorporation of volatile flavour ingredients, heat sensitive vitamins and high value nutritional powders, such as fruit or milk, without damage to their quality. Further, use of a relatively long duration treatment at modest temperature is favoured, particularly with a piece of substantial size, since this helps to alleviate unwanted inhomogeneity of sintering through the piece caused by the inevitable temperature gradient during heating.

During the sintering heat treatment, the finely dispersed glass particles acquire sufficient mobility to wet and bond neighbouring particles in contact and so achieve a 3-dimensional network structure through the whole mass.

In an alternative embodiment, a short-duration, high temperature exposure may be used to sinter-fuse the outer surface of the piece leaving the inner contents unbound. In this alternative embodiment, treatment for powder filled into a vessel with a thin-walled heat-conductive wall, such as a 33 mm diameter metal tube, would be at 90 to 110 °C for 1 to 10 minutes followed by immediate force cooling to an ambient temperature of approximately 20 °C. Preferably the sintering treatment is carried out at about 100 °C for 5 minutes before the immediate force cooling. This results in a composition in which the dry particulates are bound by a finely dispersed glassy phase at the outer surface of the solid piece beverage composition only, leaving the inner dry particulate

contents unbound. This allows even more rapid dispersal and dissolution of the particles upon contact with water.

After sintering, the product and mould are preferably allowed to cool to ambient temperature. The sintering process causes a modest contraction of the product in three dimensions such that the piece releases from the walls of the container and can be readily removed for use.

Care should be taken to protect the powders and finished product from moisture gain from the atmosphere.

Examples

The following examples are illustrative of the products and methods of making the same falling within the scope of the present invention. They are not to be considered in any way limitative of the invention. Changes and modifications can be made with respect to the invention. That is, the skilled person will recognise many possible variations in these examples covering a wide range of compositions, ingredients, processing methods, and mixtures, and can adjust the naturally occurring levels of the compounds of the invention for a variety of applications.

Example 1

In this example PowerBar® Endurance Sport Drink powder mix is bonded to make a solid form by the agency of a finely dispersed sugar glass and a thermal treatment.

PowerBar® Endurance Sport Drink mix is distributed by Powerbar Inc., Berkeley, California, 94704, USA.

A sugar glass is manufactured by dissolving and concentrating by boiling a mixture of:

Sucrose	40%,
42DE Glucose Syrup (Corn Syrup) @ 81 % dry substance	45%
Water	15%

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This operation is performed in a stirred steam-heated confectionery boiling kettle equipped with the facility to draw a partial vacuum. The mass is boiled at atmospheric pressure to a temperature maximum of 145 °C before application of a vacuum of 0.3 Bar_g until boiling stops. The resulting hot syrup is poured onto a metal slab at 20 °C and allowed to cool to ambient temperature to become hard and glassy before onward use.

A dry powder mix is prepared by co-comminution of 4 parts PowerBar® Endurance Sport Drink mix with 1 part of the sugar glass in a benchtop impact mill (Type: IKA M20 from IKA Werke GmbH & Co. KG, Staufen, Germany). Milling is continued long enough to assure that all material passes though a 1mm sieve. In fact, microscopic examination reveals particles to have a wide size range falling primarily in the band 10 to 100 microns diameter.

A dose of this dry powder mix (typically 50 g) is filled into a slightly conical rigid plastic container (105 mm length, 33 mm mid-height internal diameter, open end widest), and this is sealed with a closely fitting plastic cap to prevent moisture loss. The container and its contents are then subject to a thermal treatment by placement in a cabinet controlled at 50 °C for a period of 4 hours. After heat treatment the tube and contents are allowed to cool freely to ambient room temperature.

During the sinter heat treatment, which is performed above the glass transition of the sugar glass, the finely dispersed sugar glass particles acquire sufficient mobility to wet and bond neighbouring particles in contact and so achieve a 3-dimensional network structure through the whole mass. This process is accompanied by a modest contraction in three dimensions such that the piece releases from the walls of the container and can be readily removed for use.

The resulting body has a density of 0.7 grams per cubic centimetre and a porosity of 55 %. On addition to cold water at 15 °C the solid piece disintegrates within 10 seconds into a dispersed powder which then freely dissolves in the water.

Claims

1. A sintered, solid piece, water soluble or water dispersible beverage composition comprising dry particulates bound by a finely dispersed glassy phase which comprises 10 to 40 wt % of the composition.

2. A composition according to claim 1 having a density of 0.5 g/cm^3 to 1.0 g/cm^3.

3. A composition according to claim 2 having a density of about 0.7 g/cm^3.

4. A composition according to any of the preceding claims having a porosity of 35 % to 70 %.

5. A composition according to claim 4 having a porosity of about 55 %.

6. A composition according to any of the preceding claims wherein the dry particulates comprise one or more of crystalline sugars, maltodextrin, protein powders, cereal components, fruit powders, powdered gum, cocoa, coffee powder, tea powder, herbs, heat sensitive ingredients, and low-density inclusions which float to the surface of the beverage after dispersion.

7. A composition according to any of the preceding claims wherein the glassy phase comprises a sugar or sugar-free carbohydrate material.

8. A composition according to claim 7 wherein the glassy phase comprises corn syrup solids or dextrins or two or more of sucrose, dextrose, fructose, maltose, lactose, corn syrup solids, dextrins, sorbitol, isomalt, maltitol, xylitol, erythritol, and polydextrose.

9. A composition according to any of the preceding claims wherein the proportion of glassy phase material is in the range 15 to 25 wt %.

10. A composition according to any of the preceding claims which has a disintegration rate of <10 seconds for 50 g of sample of any dimensions in 500 ml of water at 15 °C.

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11. A composition according to any of the preceding claims wherein the solid piece composition is a dose-sized portion.

12. A composition according to any of the preceding claims wherein the dry particulates are bound by a finely dispersed glassy phase at the outer surface of the solid piece beverage composition only, leaving the inner dry particulate contents unbound.

13. A method for producing a solid piece, water soluble or water dispersible beverage composition comprising:

(a) providing a powder comprising 10 to 40 wt % glassy phase particles and 60 to 90 wt % one or more other dry particulate components; and

(b) sintering the powder, such that the glassy phase particles melt at their surface and wet and bond neighbouring particles to form a structured, porous, fused product.

14. A method according to claim 13 wherein the glassy phase particles have been milled to a fine powder prior to mixing with the dry particulate component(s).

15. A method according to claim 13 wherein the glassy phase particles and the dry particulate component(s) are mixed and then co-milled to a fine powder.

16. A method according to any of claims 13 to 15 wherein the sintering treatment is carried out at 50 to 60 °C for 5 to 10 hours.

17. A method according to any of claims 13 to 15 wherein the sintering treatment is carried out at 90 to 110 °C for 1 to 10 minutes, followed by immediate force cooling to an ambient temperature of approximately 20 °C.

18. A method according to claim 17 wherein the sintering treatment is carried out at about 100 °C for 5 minutes, followed by immediate force cooling to an ambient temperature of approximately 20 °C.

19. A method according to any of claims 13 to 18 wherein the dry particulates comprise one or more of crystalline sugars, maltodextrin, protein powders, cereal components, fruit powders, powdered gum, cocoa, coffee powder, tea powder, herbs, heat sensitive ingredients, and low-density inclusions which float to the surface of the beverage after dispersion.

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20. A method according to any of claims 13 to 19 wherein the glassy phase comprises a sugar or sugar-free carbohydrate material.

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21. A method according to claim 20 wherein the glassy phase comprises corn syrup solids or dextrins or two or more of sucrose, dextrose, fructose, maltose, lactose, corn syrup solids, dextrins, sorbitol, isomalt, maltitol, xylitol, erythritol and polydextrose.

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22. A method according to any of claims 13 to 21 wherein the proportion of glassy phase material in the composition is in the range 15 to 25 wt %.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/053146

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23F3/32 A23F5/38 A23L1/40 A23L2/395 A23P1/02
A23P1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23F A23L A23P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 July 2008	21/07/2008

Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
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EFS ID:	21949350
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
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Attorney Docket Number:	4585-101 CIP
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Application Type:	Utility under 35 USC 111(a)

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	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

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☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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	Attorney Docket Number	4585-101-CIP

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4936901	A	1990-06-26	Surgant, J., et al.	
	2	5227017	A	1993-07-13	Tanaka, T., et al.	
	3	5759599	A	1998-06-02	Wampler, D., et al.	
	4	4724121	A	1988-02-09	Weyand, J.	
	5	7332468	B2	2008-02-19	Widder, S., et al.	
	6	4525364	A	1985-06-25	Wiegers, W., et al.	
	7	4522765	A	1985-06-11	Wiegers, W., et al.	
	8	4072570	A	1978-02-07	Williams, W.	

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	9	4539209	A	1985-09-03	Wilson, R., et al.	
	10	4629586	A	1986-12-16	Wilson, R., et al.	
	11	3805869	A	1974-04-23	Winter, H., et al.	
	12	5391647	A	1995-02-21	Yamamoto, N., et al.	
	13	5137741	A	1992-08-11	Zampino, M., et al.	
	14	7090832	B2	2006-08-15	Zanone, J., et al.	

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	1	20090110796	A1	2009-04-30	Backes, M., et al.	
	2	20110064783	A1	2011-03-17	Bang-Madsen, B., et al.	
	3	20080008801	A1	2008-01-10	Barnekow, R., et al.	

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	4	20080057175	A1	2008-03-06	Barnekow, R., et al.	
	5	20080107786	A1	2008-05-08	Barnekow, R., et al.	
	6	20070166185	A1	2007-07-19	Bartels, F.	
	7	20080063747	A1	2008-03-13	Boghani, N., et al.	
	8	20050209443	A1	2005-09-22	Bolen, P., et al.	
	9	20030082272	A1	2003-05-01	Bouwmeesters, J., et al.	
	10	20090081140	A1	2009-03-26	Brocke, C., et al.	
	11	20100196493	A1	2010-08-05	Buisson, P.	
	12	20080241322	A1	2008-10-02	Bunge, R	
	13	20070231424	A1	2007-10-04	Castro, A., et al.	
	14	20030003212	A1	2013-01-02	Chien, M., et al.	

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	15	20080199592	A1	2008-08-21	Fexer, W., et al.	
	16	20110059205	A1	2011-03-10	Gaysinsky, S., et al.	
	17	20040253343	A1	2004-12-16	Ha, Y., et al.	
	18	20030196957	A1	2003-10-23	Henningfield, T., et al.	
	19	20140205713	A1	2014-07-24	Hans, K., et al.	
	20	20080064625	A1	2008-03-13	Holscher, B.	
	21	20080081779	A1	2008-04-03	Holscher, B.	
	22	20060264130	A1	2006-11-23	Karles, G., et al.	
	23	20030192815	A1	2003-10-16	Kelly, A.	
	24	20030205629	A1	2003-11-06	Kelly, A.	
	25	20070297993	A1	2007-12-27	Kindel, G., et al.	

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	26	20040062845	A1	2004-04-01	Krawczyk, G., et al.	
	27	20060159818	A1	2006-07-20	Kunieda, S.	
	28	20090124701	A1	2009-05-14	Langer, K., et al.	
	29	20090155445	A1	2009-06-18	Le, A., et al.	
	30	20070078071	A1	2007-04-05	Lee, K., et al.	
	31	20090163403	A1	2009-06-25	Levorse, Jr., A., et al.	
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	33	20080113073	A1	2008-05-15	Ley, J., et al.	
	34	20080214675	A1	2008-09-04	Ley, J., et al.	
	35	20080220140	A1	2008-09-11	Ley, J., et al.	
	36	20080227866	A1	2008-09-18	Ley, J., et al.	

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Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	6649267	B2	2003-11-18	Agawa, T., et al.	
	2	4931203	A	1990-06-05	Ahmed, F., et al.	
	3	6058624	A	2000-05-09	Bach, P., et al.	
	4	4762636	A	1988-08-09	Balliello, P., et al.	
	5	4032465	A	1977-06-28	Bauer, H., et al.	
	6	8939388	B1	2015-01-27	Beetz, C., et al.	
	7	6607771	B2	2003-08-19	Benczedi, D., et al.	
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	9	5786017	A	1998-07-28	Blake, A., et al.	
	10	RE37860	E	1998-07-28	Blake, A., et al.	
	11	4962089	A	1990-10-09	Boden, R., et al.	
	12	4539143	A	1985-09-03	Boden, R., et al.	
	13	4677207	A	1987-06-30	Boden, R., et al.	
	14	4950495	A	1990-08-21	Boden, R., et al.	
	15	4568538	A	1986-02-04	Boden, R., et al.	
	16	4983579	A	1991-01-08	Boden, R., et al.	
	17	4883884	A	1989-11-28	Boden, R., et al.	
	18	4515987	A	1985-05-07	Boden, R., et al.	
	19	4422900	A	1983-12-27	Bordelon, K., et al.	

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	20	5124162	A	1992-06-23	Boskovic, M., et al.	
	21	6929814	B2	2005-08-16	Bouwmeesters, J., et al.	
	22	5004618	A	1991-04-02	Buckholz, Jr., L., et al.	
	23	3817308	A	1974-06-18	Bundo, T.	
	24	3962384	A	1976-06-08	Cannalonga, M., et al.	
	25	6962006	B2	2005-11-08	Chickering, III., D., et al.	
	26	6560897	B2	2003-05-13	Chickering, D., et al.	
	27	5593715	A	1997-01-14	Christensen, M.	
	28	7022665	B2	2006-04-04	Decorzant, R., et al.	
	29	5354742	A	1994-10-11	Deming, J., et al.	
	30	6482433	B1	2002-11-19	DeRoos, K., et al.	

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	31	6325859	B1	2001-12-04	De Roos, K., et al.	
	32	7361376	B2	2008-04-22	Dewis, M., et al.	
	33	7534460	B2	2009-05-19	Dewis, M., et al.	
	34	7097872	B2	2006-08-29	Dewis, M., et al.	
	35	3554768	A	1971-01-12	Feldman, J.	
	36	3677321	A	1972-07-18	Felstead, E.	
	37	4532364	A	1985-07-30	Fujioka, F., et al.	
	38	4521634	A	1985-06-04	Fujioka, F., et al.	
	39	4544775	A	1985-10-01	Fujioka, F., et al.	
	40	4619780	A	1986-10-28	Fujioka, F., et al.	
	41	6689755	B1	2004-02-10	Gabel, R., et al.	

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	42	6387431	B1	2002-05-14	Gautschi, M.	
	43	7252848	B2	2007-08-07	Gelin, J.	
	44	5773061	A	1998-06-30	Getler, J., et al.	
	45	6048565	A	2000-04-11	Getler, J., et al.	
	46	6077543	A	2000-06-20	Gordon, M., et al.	
	47	3844969	A	1974-10-29	Griffiths, J., et al.	
	48	3840996	A	1974-10-15	Grindstaff, D., et al.	
	49	5445839	A	1995-08-29	Hagiwara, Y., et al.	
	50	4520032	A	1985-05-28	Hall, J., et al.	

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	1	0420509	EP	A1	1991-04-03	Arora, V., et al.		☐
	2	9714288	WO	A2	1997-04-24	Bach, P., et al.		☐
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14606771
	Filing Date	2015-01-27
	First Named Inventor	Beetz
	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	9	1064856	EP	A2	2001-01-03	De Ross, K., et al.		☐
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	11	2253154	CA	C	1999-05-03	Gabel, R., et al.		☐
	12	1162699	CA	A	1984-02-21	Gagliani, J., et al.		☐
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	19	549614	AU	B2	1986-02-06	Hsu, J.		☐

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	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	20	0227486	EP	B1	1991-11-27	Iwaya, S., et al.		☐
	21	2364714	GB	A	2002-02-06	James, M., et al.		☐
	22	0366898	EP	B1	1996-02-07	Kasica, J., et al.		☐
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	25	0429482	EP	B1	1994-04-06	Mitchell, C., et al.		☐
	26	2407614	CA	C	2001-11-08	Mizuguchi, T., et al.		☐
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	28	2005063032	WO	A1	2005-07-14	Mysore, N., et al.		☐
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	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

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	Art Unit	3752
	Examiner Name	
	Attorney Docket Number	4585-101-CIP

	1	BAILEY, A., "Electrostatic Spraying of Liquids", April 1988, Page(s) 1-35, Publisher: Research Studies Press Ltd., Published in: Taunton, Somerset, England	☐
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	10	NOTE: For the non-patent literature citations that no month of publication is indicated, the year of publication is more than 1 year prior to the effective filing date of the present application.	☐

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	Art Unit	3752
	Examiner Name	
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	Examiner Name	
	Attorney Docket Number	4585-101-CIP

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/steven j. hultquist/	Date (YYYY-MM-DD)	2015-04-02
Name/Print	Hultquist, Steven J.	Registration Number	28021

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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Bibliographic data: AU549614 (B2) — 1986-02-06

FERMENTED VEGETABLE - HYDROLYSED PROTEIN FLAVOURANT

Inventor(s): HSU JAU YANN ± (JAU YANN HSU)

Applicant(s): NESTLE SA ± (SOCIETE DES PRODUITS NESTLE S.A)

Classification: **- international:** ***A23B7/10; A23L1/22; A23L1/221; A23L1/23; A23L1/27;*** (IPC1-7): A23L1/212; A23L1/23
- cooperative: **A23B7/105**; **A23L1/221**; **A23L1/23**; **A23L1/27**

Application number: AU19830010003 19830104

Priority number (s): US19820353393 19820301

Also published as: EP0087522 (A1) EP0087522 (B1) EP0087522 (B2) PH17877 (A) OA7329 (A) more

Abstract not available for AU549614 (B2)
Abstract of corresponding document: EP0087522 (A1)

A flavouring composition comprising a mixture prepared a) from 10 to 80 % by weight of a fermented vegetable juice and from 20 to 90 % by weight of a hydrolysed protein based on the weight of the mixture or b) from 2 to 80 % by weight of a dehydrated fermented vegetable and from 20 to 98 % by weight of a hydrolysed protein based on the weight of the mixture. Flavouring agents with appetizing sour notes and with meat and vegetable flavour characteristics are described.



(12) AUSTRALIAN PATENT ABRIDGMENT
(19) AU (11) AU-B-10003/83

(54) FERMENTED VEGETABLE - HYDROLYSED PROTEIN FLAVOURANT

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952-69
FORM 10
549614
10003/83
MICROCOPY RESOLUTION TEST CHART

10003/83

FORM 1

549614

REGULATION 9 (1)

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1979

APPLICATION FOR A STANDARD PATENT

We, SOCIÉTÉ DES PRODUITS NESTLÉ S.A., a Swiss Company of Vevey, Switzerland, hereby apply for the grant of a standard patent for an invention entitled:-

"FLAVOURING COMPOSITIONS"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 353,393

Country: U.S.A.

Date: 1st March, 1982.

Our address for service is:-

SHELSTON WATERS,
55 Clarence Street,
SYDNEY. N.S.W. 2000.

DATED this 4th day of JANUARY, 1983.

SOCIÉTÉ DES PRODUITS NESTLÉ S.A.

LODGED AT SUB-OFFICE
Sydney

by Robert H. Shelston

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

55

To: The Commissioner of Patents,
WODEN. A.C.T.

File: D.B. 40H gf

Fee: $ 55.00

LODGED AT SUB-OFFICE
PATENT OFFICE
1983
Sydney





COMMONWEALTH OF AUSTRALIA

PATENTS ACT, 1952-1973

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convertion Application No. ..... made by [a] Société des Produits Nestlé S.A. .....

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

[b] "Flavouring compositions"

I, [c] Andrzej W. Ledzion

of [d] En la Priauraz, 1807 BLONAY, Switzerland

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was/were made in [e] the United States of America on the 1st day of March 1982 on the ..... day of ..... 19..... by [f] Jau Yann HSU

3. [g] Jau Yann HSU

of 21, Flax Hill Road, BROOKFIELDS, 06804 Connecticut, U.S.A. is/are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

Applicant is the Assignee of the said Inventor(s).

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at Vevey, Switzerland

this 27th day of December 1982

[h] .....

(Signature of Declarant)

To THE COMMISSIONER OF PATENTS.

(a) Here insert (in full) Name of Company.

(b) Here insert Title of Invention.

(c) and (d) Here insert Full Name and Address of Company Official authorised to make declaration.

(e) Here insert Basic Country or Countries followed by date or dates of Basic Application(s).

(f) Here insert Full Name(s) of Applicant(s) in Basic Country.

(g) Here insert (in full) Name and Address of actual Inventor or Inventors.

(h) Personal Signature of Declarant (c) (no seal, witness or legalisation).

SHELSTON WATERS
PATENT ATTORNEYS
55 CLARENCE STREET, SYDNEY
AUSTRALIA
Cables: 'Valid' Sydney Telex: 24422

(12) AUSTRALIAN PATENT ABRIDGMENT
(19) AU (11) AU-B-10003/83

(54) FERMENTED VEGETABLE - HYDROLYSED PROTEIN FLAVOURANT

(71) SOCIETE DES PRODUITS NESTLE S.A.
(21) 10003/83 540614 (22) 4.1.83
(24) 1.3.82
(31) 353393 (32) 1.3.82 (33) US
(43) 8.9.83 (44) 6.2.86
(51)3 A23L 1/23 A23L 1/212
(72) JAU YANN HSU
(74) SW
(56) 91393/82 A23L
91630/82 A23B

(57) Claim

1. A flavouring composition characterised in that it comprises a mixture prepared

a) from 10 to 80 % by weight of a fermented vegetable juice and from 20 to 90 % by weight of a hydrolysed protein based on the weight of the mixture or

b) from 2 to 80 % by weight of a dehydrated fermented vegetable and from 20 to 98 % by weight of a hydrolysed protein based on the weight of the mixture.

116/60/20

10003

COMP

Application Number:
Lodged:

Complete Specification Lod
Accep
Publis

Priority:

Related Art:

Name of Applicant: SO

Address of Applicant:

Actual Inventor:

Address for Service: Shelsto

Complete Specification for t

The following statement is
known to me/us:—

10003/83

549614

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

FOR OFFICE USE:

Class Int. Class

Application Number: 10003/83
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: SOCIÉTÉ DES PRODUITS NESTLÉ S.A.

Address of Applicant: Vevey, Switzerland.

Actual Inventor: JAU YANN HSU

Address for Service: Shelston Waters, ~~163~~ 55 Clarence Street, Sydney

Complete Specification for the Invention entitled: "FLAVOURING COMPOSITIONS"

The following statement is a full description of this invention, including the best method of performing it known to me/us:—

SW16

Flavouring Compositions

The present invention relates to flavouring compositions more particularly to mixtures containing fermented vegetables and hydrolysed proteins.

Hydrolysed proteins which are used as flavouring agents may be either chemically hydrolysed or enzymatically hydrolysed. Chemically hydrolysed proteins do not have the fermented flavour characteristic of enzymatically hydrolysed proteins because, unlike the latter, they do not contain alcohols, sugars, lactic acid and acetic acid. In order to impart an appetizing sour note to hydrolysed plant protein, acidulants such as lactic acid, acetic acid or citric acid are commonly used. We have found, surprisingly, that by mixing fermented vegetables (solid or juice) with chemically or enzymatically hydrolysed proteins an appetizing sour note and a meat and vegetable flavour is imparted thereto, this flavour enhancing and modification effect being stronger and different from that imparted by the regular acidulants. Moreover, the admixture of fermenced vegetables with chemically hydrolysed proteins creates fermented flavours similar to those of enzymatically hydrolysed proteins.

Accordingly, the present invention provides a flavouring composition comprising a mixture prepared

a) from 10 to 80 % by weight of a fermented vegetable juice and from 20 to 90 % by weight of a hydrolysed protein based on the weight of the mixture or

b) from 2 to 80 % by weight of a dehydrated fermented vegetable and from 20 to 98 % by weight of a hydrolysed protein based on the weight of the mixture.

In the flavouring compositions formed from either of the mixtures a) and b) the hydrolysed protein may be in either

liquid or powder form.

The fermented vegetable may be any vegetable preserved by lactic acid fermentation for example, fermented vegetables prepared from cabbage, cucumber, green tomato, red pepper, mustard stem, mustard green, radish, turnip or squash.

The hydrolysed protein may be of plant or animal origin and may be a chemically or enzymatically hydrolysed protein. For example, the hydrolysed protein may be a chemical hydrolysate prepared from a plant or animal source, an autolysed yeast extract from brewer's or baker's yeast, soy sauce from enzymatically degraded soy or soy and wheat mixtures, and meat flavours based on hydrolysed proteins reacting with other ingredients such as reducing sugars, thiamine or cysteine.

In one example of a fermented flavour prepared from a mixture of type a), the flavouring composition may be a hydrolysed protein liquid seasoning which comprises a mixture of fermented vegetable juice and chemically hydrolysed protein which is preferably in the form of a powder or paste. The mixture preferably contains from 15 to 75 % and especially from 20 to 70 % by weight of fermented vegetable juice, the remainder being hydrolysed protein. Optionally, other ingredients such as salt and water may be added depending on the desired fermented flavour intensity and saltiness. If desired the fermented vegetable juice may be concentrated or concentrated and dried before mixing with the chemically hydrolysed protein. Alternatively, the fermented vegetable juice and chemically hydrolysed protein may be dried, conveniently by spray-drying whereby only a small amount of the volatile acids are lost, advantageously at a temperature of from 85°C to 95°C, and used as a powdered flavouring agent.

In another example of a fermented flavour prepared from a

mixture of type a), the flavouring composition may be a liquid seasoning with a fermented soy sauce flavour characteristic which comprises a mixture of fermented vegetable juice and a reaction liquid formed by heating glucose and water with a chemically hydrolysed protein containing chemically hydrolysed soy protein in an amount generally from 25 to 75 % by weight of the total hydrolysed protein. The amount of fermented vegetable juice in the mixture is conveniently from 15 to 60 % and especially from 20 to 50 % by weight based on the weight of the composition, the remainder being the chemically hydrolysed protein/glucose reaction liquid. Examples of fermented vegetable juices which may be used are sauerkraut and fermented cucumber juices.

In a flavour prepared from a mixture of type b) having meat, vegetable or cooked acid properties, the flavouring composition is preferably a powder which comprises a mixture of a powdered dehydrated fermented vegetable and either a powdered hydrolysed protein or a powdered meat flavour based on hydrolysed protein. The protein may be chemically or enzymatically hydrolysed.

The fermented vegetables used may be fermented mustard stem, mustard green, cabbage, radish or pickled cucumber. The fermented vegetables are conveniently dehydrated by vacuum drying, drum drying or hot air drying. Vacuum drying may be conducted in shelf dryers. The fermented vegetables may be in normal or frozen condition and the drying temperature may be from 70°C to 90°C under a vacuum of for example, from 25 mm to 30 mm Hg. In hot air or drum drying, the drying temperature is preferably from 120°C to 150°C. Hot air drying can be carried out in a tray or a fluidised bed. Drum drying can be carried out under atmospheric or vacuum conditions. The drying time depends on the moisture content which, after drying, is preferably below 10 % by weight and especially

below 5 % by weight. Vacuum drying is preferred because of the lower drying temperatures used which minimise the loss of volatile acids. After drying, the vegetables may then be ground into the powder which is preferably fine.

The hydrolysed protein may be a chemically hydrolysed protein from plant or animal sources, autolysed yeast extracts from brewer's or baker's yeast and soy sauce from enzymatically degraded soy or soy and wheat mixtures. The protein may be dried in a similar manner to the fermented vegetables.

The fermented vegetables and the hydrolysed proteins are preferably dried separately and then mixed together to form a meat/vegetable stock flavour ingredient. The amount of dehydrated fermented vegetable present is conveniently from 5 to 65 % and preferably from 10 to 60 % by weight based on the weight of the mixture, the remainder being the hydrolysed protein. This flavour mixture may be rehydrated with hot water to give an instant broth.

If desired, however, the fermented vegetables and hydrolysed proteins may be dried together to produce a cooked vegetable flavour. The amount of dehydrated fermented vegetable present in such a flavour may be from 5 to 65 % and preferably from 10 to 60 % by weight based on the weight of the mixture, the remainder being the hydrolysed protein. This flavour mixture may be rehydrated with hot water to give a cooked acid/vegetable flavour that can be used in instant dishes.

The present invention also provides a powdered dehydrated fermented vegetable which may be used as a flavouring agent.

The following Examples further illustrate the present invention. Parts are expressed by weight.

Example 1

38 parts of powdered chemical hydrolysate were mixed with 62 parts sauerkraut juice and the mixture was spray-dried in a Niro spray dryer (inlet temperature: 88-93°C., outlet temperature: 32-35°C.). The spray dried powder had a natural fermented flavour characteristic and the acid taste was also stronger than that of chemical hydrolysate because of the incorporation of lactic acid from juice to hydrolysate as indicated by the following analytical results (5 % solution):

	Acidity	pH
Chemical Hydrolysate Powder	5.94 %	5.2
Spray Dried Powder of Chemical Hydrolysate and Sauerkraut Juice	7.92 %	4.2

Example 2

10 parts of powdered soy chemical hydrolysate, 10 parts of powdered wheat chemical hydrolysate, 3 parts of glucose and 4.6 parts of salt were heated with 28 parts of water at 80-85°C. for one hour. To this mixture were added 5 further parts of powdered soy chemical hydrolysate, 5 further parts of powdered wheat chemical hydrolysate and 34.4 parts sauerkraut juice. The resultant liquid had a fermented flavour characteristic similar to that of fermented soy sauce.

Example 3

Liquid bottle seasoning was concentrated and vacuum dried into powder form and 40 parts of this dehydrated bottle seasoning was added to 60 parts of sauerkraut juice. Compared with regular bottle seasoning, the powdered seasoning rehydrated with sauerkraut juice had a refreshing flavour

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Example 4

Fermented mustard stem was dehydrated into dry form under vacuum at 80°C for 3 hours until the moisture content was below 5 %, and then ground into fine powder form. 50 parts of this powder was added to 50 parts of powdered soy sauce to give the flavouring mixture. When this mixture was rehydrated with hot water, an instant broth was formed which had a typical flavour characteristic of Oriental fermented vegetable/meat broth.

Example 5

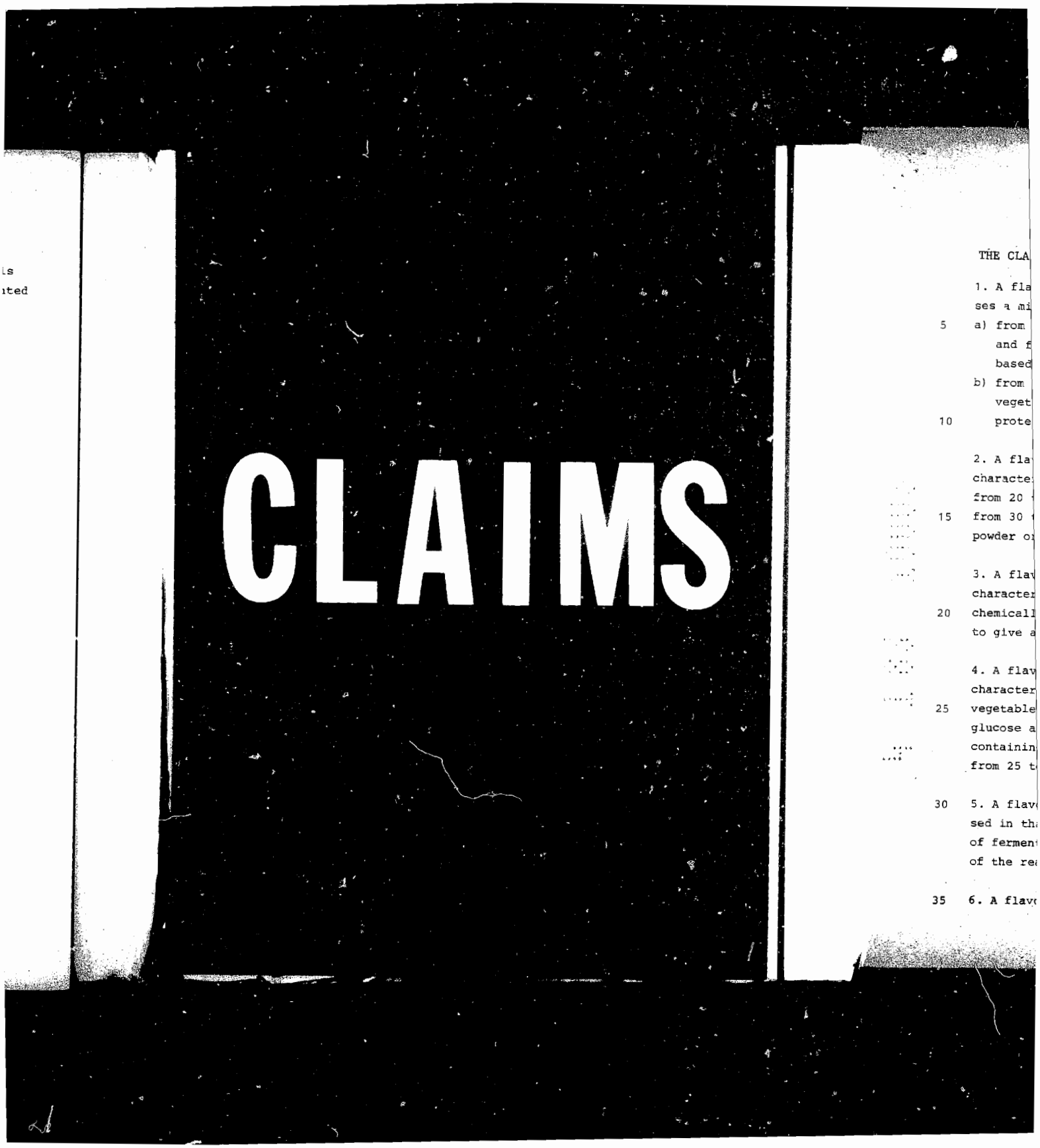
70 parts of sauerkraut (solids and juice) was ground into a fine paste and mixed with 30 parts of hydrolysed protein paste. This mixture was dehydrated under vacuum at 80°C for 4 hours to give a dry form having a moisture content below 5 % and then ground to a fine powder. When this mixture was rehydrated with hot water a cooked acid/vegetable flavour was produced which could be used in instant food dishes.

Example 6

Sauerkraut was dehydrated under vacuum at 80°C to a moisture content below 5 %. 0.2 g of the dehydrated sauerkraut (containing 12 % lactic acid) was added to 1.0 g hydrolysed plant protein in 170 ml of hot water. The mixture had a strong appetizing vegetable note.

In comparison, when a similar process was carried out but using 0.2 g lactic acid powder (containing 22 % lactic acid) instead of the dehydrated sauerkraut, the flavour was weaker

and not very different from hydrolysed plant protein. This indicates that the flavouring effect of dehydrated fermented vegetable is not contributed solely by its lactic acid content.



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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A flavouring composition characterised in that it comprises a mixture prepared

a) from 10 to 80 % by weight of a fermented vegetable juice and from 20 to 90 % by weight of a hydrolysed protein based on the weight of the mixture or

b) from 2 to 80 % by weight of a dehydrated fermented vegetable and from 20 to 98 % by weight of a hydrolysed protein based on the weight of the mixture.

2. A flavouring composition of type a) according to claim 1 characterised in that it comprises a mixture containing from 20 to 70 % by weight of fermented vegetable juice and from 30 to 80 % by weight of chemically hydrolysed protein powder or paste based on the weight of the mixture.

3. A flavouring composition of type a) according to claim 1 characterised in that the fermented vegetable juice and chemically hydrolysed protein are dehydrated by spray drying to give a powder.

4. A flavouring composition of type a) according to claim 1 characterised in that it comprises a mixture of fermented vegetable juice and a reaction liquid formed by heating glucose and water with a chemically hydrolysed protein containing chemically hydrolysed soy protein in an amount from 25 to 75 % by weight of the total hydrolysed protein.

5. A flavouring composition according to claim 4 characterised in that the mixture contains from 20 to 50 % by weight of fermented vegetable juice and from 50 to 80 % by weight of the reaction liquid based on the weight of the mixture.

6. A flavouring composition of type b) according to claim 1

characterised in that it comprises a mixture of powdered dehydrated fermented vegetable and either a powdered hydrolysed protein or a powdered meat flavour based on hydrolysed protein, the protein being chemically or enzymatically hydrolysed.

7. A flavouring composition according to claim 6 characterised in that the fermented vegetables and hydrolysed proteins are dehydrated by vacuum drying.

8. A flavouring composition according to claim 6 or claim 7 characterised in that the fermented vegetables and the hydrolysed proteins are dried separately and then mixed to give a mixture containing from 5 to 65 % by weight of dehydrated fermented vegetables and from 35 to 95 % by weight of hydrolysed protein based on the weight of the mixture.

9. A flavouring composition according to claim 6 or claim 7 characterised in that the fermented vegetables and the hydrolysed proteins are dried together to give a solid mixture containing from 5 to 65 % by weight of dehydrated fermented vegetables and from 35 to 95 % by weight of hydrolysed proteins based on the weight of the mixture.

~~10. A powdered dehydrated fermented vegetable.~~

DATED this 4th day of JANUARY, 1983

SOCIÉTÉ DES PRODUITS NESTLÉ S.A.

Attorney: ROBERT C. SHELSTON
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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(54) METHODS OF PREPARING POLYIMIDES AND POLYIMIDE PRECURSORS

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ABSTRACT OF THE DISCLOSURE

Methods of preparing polyimides and polyimide precursors from liquid resins containing tetracarboxylic acid esters and primary diamines which involve spray drying the resin.

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METHODS OF PREPARING POLYIMIDES AND POLYIMIDE PRECURSORS

Our invention relates to polyimides and, more particularly, to novel, improved methods for preparing polyimides and dry, particulate precursors which can be converted into polymers of that character.

One class of polymers that is receiving increasing attention as criteria for structural materials become more demanding from a variety of viewpoints is the family of compounds known as polyimides.

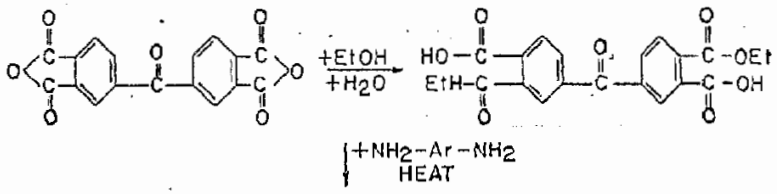
As a class, polyimides are extremely valuable materials because of their chemical inertness, strength, and temperature resistance. There are also certain classes proprietary polyimides which have such additional advantages such as retention of strength and resiliency and flexibility at cryogenic temperatures; resistance to hydrolysis and ultraviolet degradation; capability of undergoing oxidative degradation without generating toxic products or smoke; a novel closed cell structure which suits them for applications in which they are in contact with moving parts; the capacity to be transformed into porous fibers and other shapes and into rigid panels, cushioning, thermal acoustical insulation and a host of other novel products. These polyimides are disclosed in, inter alia, U.S. patents Nos. 3,506,583 issued April 14, 1970, to Boram et al; 3,726,831 and 3,726,834 issued April 10, 1973, to Acle et al. and Acle, respectively; 4,070,312 issued January 24, 1978, to Gagliani et al; and Re 30,213 issued February 12, 1980, to Gagliani and in U.S. Patent No. 4,241,193 issued December 23, 1980 and Canadian Patent No. 1,132,320 issued September 28, 1982 to Gagliani, and Canadian application Serial No. 385,181, filed September 3, 1981 by Gagliani.

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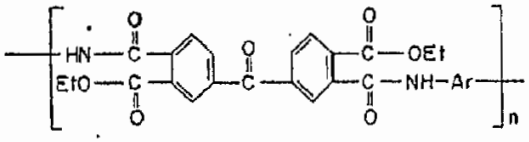
These proprietary polyimides are prepared by reacting 3,3', 4,4'-benzophenonetetracarboxylic acid or a dianhydride of that acid with a lower alkyl alcohol to form a half ester of the acid and then adding one or more primary diamines to the half ester solution to form an essentially monomeric precursor. Dielectric, thermal, or microwave heating is employed to convert the precursor to a polyimide.

The general model for the chemical reactions which are effected in converting the precursor to a polyimide are shown below. The actual reactions are typically much more complex depending upon the number of diamines in the precursor.

(i) Esterification:

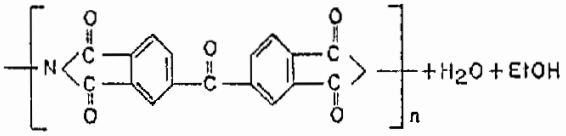


(ii) Amidization:





(iii) Imidization:



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The material existing after dissolution of the diamines and the addition of any additives is what we term a "liquid resin". The material may be used in that form. However, in many cases--for example in making polyimide foams of the character described in reissue patent No. 30,213--it is often advantageous to first convert the precursor to a dry, particulate form. Ease of handling, as an example, is one advantage of the dry precursors.

Typically, this has heretofore been accomplished by heating the liquid resin in a circulating air oven at 65.6 to 87.8°C (150 to 190°F) for 12-16 hours. This is followed by drying in a vacuum oven at a temperature of 60.0 to 76.7°C (140 to 170°F) and an absolute pressure of 33.4 to 3.3 kPa (10 to 1.0 in. of Hg) for 60-120 minutes. Thereafter, the dried material is crushed, pulverized, and sieved.

The foregoing technique for converting the liquid resin to a dry, particulate precursor is time consuming and correspondingly expensive; the foams tend to be non-homogeneous; and the results are often not reproducible. Also, the time required for the drying steps makes it impractical to manufacture the particulate powder by continuous as opposed to batch-type processes. This is also an important economic drawback, especially in making precursors on a large scale.

We have now discovered that precursors of the character just described and, typically, of superior quality can be produced by employing a spray drying technique to transform the liquid tetracarboxylic acid ester/primary diamine resin into a dry powder. This technique has the additional advantage that, by varying a single process parameter, the properties of the materials into which the precursors are converted, such as the load deflection indentation of polyimide foams, can be optimized for particular applications.

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In one broad aspect, the invention pertains to a method of preparing a dry, foamable, particulate precursor which can be converted into a polyimide by heating it. The method includes the steps of forming a primary diamine, 3,3', 4,4'-benzophenonetetracarboxylic acid ester solution by dissolving one or more such diamines and the aforesaid acid or an anhydride thereof in a lower alkyl alcohol, atomizing the solution, and drying the droplets obtained by atomizing the diamine, ester solution with a heated gas.

The invention further pertains to a method of preparing a polyimide which includes the steps of forming a half ester of 3,3', 4,4'-benzophenonetetracarboxylic acid by reacting the acid or an anhydride thereof with a lower alkyl alcohol, dissolving one or more primary diamines in the half ester, alcohol solution, spray drying the material thus formed to convert it into a dry particulate polyimide precursor, and converting the precursor to a polyimide by heating it.

Exemplary of the polyimides which can be prepared to advantage by the use of spray drying in accord with the

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principles of the present invention to make the precursors are the copolymers described in U.S. Reissue patent No. 30,213 and the terpolymers described in Canadian Patent Application Serial No. 385,181, filed September 3, 1981.

The patented copolymers are derived from precursors which, in their preferred forms, are essentially equimolar mixtures of a lower alkyl half ester of 3,3', 4,4' -benzophenonetetracarboxylic acid and two diamines. One of the diamines is a heterocyclic diamine, and the other is an aromatic meta- or para-substituted diamine which is free of aliphatic moieties. A ratio of 0.4 to 0.6 mole of heterocyclic diamine per mole of 3,3',4,4'-benzophenonetetracarboxylic acid ester is preferred as this results in foams with optimal mechanical properties. However, as will become apparent hereinafter, precursors having a heterocyclic diamine/acid ester ratio of 0.3 have also successfully been employed.

The terpolyimides described in Canadian Application Serial No. 385,181 differ chemically from the copolyimides just described in that they are made from precursors which include an aliphatic diamine in addition to the aromatic and heterocyclic diamines employed in the copolyimide precursors.

From 0.05 to 0.3 mole of aliphatic diamine per 1.0 mole of benzophenonetetracarboxylic acid ester can be employed, and from 0.1 to 0.3 mole of heterocyclic diamine per mole of acid can be used.

Exemplary of the aromatic and heterocyclic diamines that can be employed in the just described copolyimides and terpolyimides are:

2,6-diaminopyridine
3,5-diaminopyridine
3,3'-diaminodiphenyl sulfone
4,4'-diaminodiphenyl sulfone
4,4'-diaminodiphenyl sulfide
3,3'-diaminodiphenyl ether
4,4'-diaminodiphenyl ether
meta-phenylene diamine

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para-phenylene diamine
p,p'-methylene dianiline
2,6-diamino toluene
2,4-diamino toluene

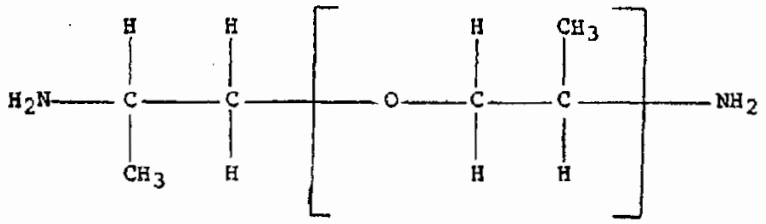
Many other aromatic and heterocyclic diamines have been described in the open and patent literature dealing with the making of polyimides--see, for example, U.S. Patents Nos. 3,179,614 issued April 20, 1965, to Edwards; 3,575,891 issued April 20, 1971, to LeBlanc et al; and 3,629,180 issued December 21, 1971, to Yoda et al. Aromatic and heterocyclic diamines selected from those listed in the literature can also be utilized in copolyimides and terpolyimides of the character described above.

Aliphatic diamines having from three to 12 carbon atoms have been employed in the terpolyimides. However, diamines having no more than six carbon atoms will typically prove preferable. Also, aliphatic diamines with even number chains are preferred.

Aliphatic diamines we have used include:

1,3-diaminopropane
1,4-diaminobutane
1,6-diaminohexane
1,8-diaminooctane
1,12-diaminododecane

and Jeffamine™ 230. The latter is available from the Jefferson Chemical Company and has the formula:



where x is approximately 2.6.

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As discussed briefly above, the precursors of the polyimides with which we are concerned are prepared by first reacting 3,3', 4,4'-benzophenonetetracarboxylic acid or, preferably, its dianhydride with an esterfication agent to form an alkyl diester. Exemplary esterfication agents are methyl, ethyl, propyl, and isopropyl alcohols. Methanol is in many cases preferred because of its widespread availability, low cost, and other attributes; because its use facilitates conversion of the precursor to a polyimide foam which is important in applications involving the manufacture of that type of material; and because the foams made from the methyl esters tend to be more flexible, resilient, and compression set resistant.

Ethanol is also a preferred esterfication agent.

The esterification reaction is followed by the addition of the diamine or diamines, which are dissolved in the reaction mixture. The temperature is kept below the reflux temperature of the esterfication agent during dissolution of the diamines and low enough to avoid polymerization of the diamines and ester.

Graphite, glass, and other fibers as well as other fillers such as glass microballoons and additives such as cross-linking agents can be added to the resulting composition to impart wanted properties to the final product. A surfactant can also be added to increase fatigue resistance of the terpolyimide foam and to make it more flexible and resilient by increasing the bubble stability of the foam and the uniformity of the cellular structure.

One preferred surfactant is FS-B, a nonionic, fluorinated, polyalkylene copolymer manufactured by E. I. DuPont de Nemours and Company.

Other surfactants that have been successfully employed are FS-C, a nonionic surfactant of the same general chemical composition as FS-B and manufactured by the same company, and L-530, L-5410, and L-5430, which are silicone surfactants manufactured by Union Carbide Company. We employ from 0.01 to 1 percent of surfactant based on the weight of the ester and diamine constituents.

The liquid resin existing after dissolution of the diamines and the addition of any additives is transformed by spray drying in accord with the principles of the present invention into an amorphous, dry powder which is an essentially unpolymerized resinoid of one or more benzophenonetetracarboxylic acid half esters and one or more diamines (preliminary tests of one copolyimide precursor of the type described above, for example indicated that the precursor had a chain length of about 20 to 30 molecules).

The amophorous, powdered, resinoid precursor can be converted into a monolithic, polyimide foam by various techniques including dielectric, thermal, and microwave heating. The latter, alone or with a thermal post-cure, is preferred because of the speed with which the foam can be developed and cured; because the foam is homogeneously heated; and because handling of the fragile, uncured foam can be avoided.

Microwave techniques and equipment that can be used to foam and cure the precursor are disclosed in U.S. Patent No. 4,305,796 issued December 15, 1981.

Foaming-curing parameters that have proven satisfactory in converting 100 gram samples of representative precursors to flexible, resilient foams are two to 12 minutes exposure to high frequency radiation in an oven operating at a frequency of 2450 MHZ and at 5KW power followed by thermal heating at a temperature of 500-550°F for 15 minutes to two hours.

The resulting foam can be employed as such -- in a seat cushion or as insulation, for example. Or, using the procedure described in U.S. Patent 4,241,193 as a further example, the flexible, resilient polyimide foam can be converted to a dense, rigid, structurally strong, intumescent material by heating it under pressure. The foam can also be comminuted and used as a molding powder as described in patent No. 3,726,834.

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From the foregoing it will be apparent to the reader that the primary aspect of the present invention resides in the provision of novel, improved methods of manufacturing polyimides and their precursors.

A related, also important and primary aspect of our invention resides in the provision of novel, improved processes for producing polyimide precursors in a dry particulate form from fluid mixtures of benzophenonetetracarboxylic acid esters and primary diamines.

Related, also important but more specific aspects of our invention reside in the provision of methods for preparing such polyimide precursors:

which can be carried out on a continuous as opposed to batch-type basis;

which make the preparation of the precursors relatively inexpensive;

which afford ready control over the mechanical properties of the polyimides into which the precursors are converted;

which are useful in preparing a wide variety of precursors of the character indentified above;

in which spray drying is employed to eliminate volatiles from the material being processed.

Other important aspects and features and additional advantages of our invention will become apparent from the appended claims and as the ensuing detailed description and discussion of our invention proceeds in conjunction with the accompanying drawing in which:

Figure 1 is a schematic illustration of spray drying apparatus for transforming a fluid mixture into a dry, particulate polyimide precursor in accord with the principles of the present invention;

Figure 2 is a schematic illustration of the operations in the reactor of the spray drying apparatus; and

Figure 3 shows, graphically, the effect on the precursor of certain variations in the spray drying process.

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Referring now to the drawing, Figures 1 and 2 depict an exemplary spray drying system 20 for preparing powdered polyimide precursors in accord with the principles of the present invention.

For the most part, the components of system 20 are of conventional, commercially available construction. For that reason and because the details of the spray drying system are not part of the present invention, that system will be described herein only to the extent necessary for an understanding of the present invention.

The major components of system 20 include a Niro Mobile Minor reactor or spray dryer 22 mounted on a stand 24. Liquid resin feedstock flows to the spray dryer from a reservoir 26 through a valve 28 which can be adjusted to control the rate of flow.

Dry powder produced in spray dryer 22 migrates to the bottom of the dryer and is kept from sticking to the interior of spray dryer casing 30 by a timed impact vibrator 32 mounted on stand 24.

The dry powder flows through an offtake conduit 34 into a cyclone separator 36 where the powdered precursor is separated from air and evolved volatiles in which it is entrained and collected in a container 38.

Aside from the components just described, spray drying system 20 includes a schematically illustrated system 40 for supporting and shifting container 38, a control panel 42, and thermometers or other instruments (not shown) for measuring the temperature at the inlet 44 and outlet 46 of spray dryer 22 (see also Figure 2).

As shown in Figure 2, the liquid resin introduced into spray dryer 22 through feedstock conduit 48 is converted into an annular spray of droplets by a rotating wheel-type atomizer 50. These droplets are entrained in a swirling annulus of heated air as they are formed. The air flows radially inward into spray dryer 22 through a ceiling air disperser 52 at the top of the spray dryer and then downwardly around the rotating wheel 58 of atomizer 50.

The air is preferably supplied at constant pressure because variations in air pressure can cause fluctuations in the speed of wheel 50; and this will effect the characteristics of the dry, particulate precursor and the polyimide into which it is converted as will be discussed hereinafter.

The interaction between the heated air and the drops of liquid resin shown in Figure 2 result in the drops being almost instantaneously dried. The resulting particles, entrained in the heated air and the solvent evolved from them, migrate downwardly to the lower end of spray dryer 22 and are discharged from the spray dryer through previously mentioned offtake conduit 34.

Because the evaporation of solvent from the liquid resin is accompanied by cooling of the droplets and because of the short residence time of the resin in the reactor, overheating of the precursor can be avoided; and more precise control over the drying process can be exercised than was possible using the prior art technique described above.

The system 20 illustrated in the drawing and just described is capable of producing dry, particulate polyimide precursors on a continuous basis, virtually without operator attention.

That our novel process for producing dry, particulate, polyimide precursors is highly efficacious was demonstrated by making such precursors in the spray drying apparatus described above from a liquid feedstock of the character with which we are concerned.

The feedstock was prepared by adding 3,3', 4,4'-benzophenonetetracarboxylic acid dianhydride (322.23 g, 1.0 mole) to 240 ml of methyl alcohol and 24 ml of H_2O in a one-liter, three neck flask equipped with a thermometer, a mechanical stirrer and a reflux condenser. After addition, the mixture was heated and refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of the acid to its half ester.

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The reaction mixture was then cooled to 40-50°C (104-122°F).

2,6 Diaminopyridine (32.8 g, 0.3 mole) and p-p'methylene dianiline (138.7 g, 0.7 mole) were added to the half ester solution, and the mixture was heated to 60-65°C (140-149°F) for five minutes.

FS-C surfactant was next added to the mixture in an amount of 0.1 percent based on the weight of the methyl half ester and the diamines.

The preparation of the liquid resin feedstock was completed by diluting the mixture with methyl alcohol in a ratio of 100 parts of half ester, diamines, and surfactant to 20 parts of alcohol (20 phr).

Next, the reactor was heated to temperatures of 100, 110, 120, or 130°C and the feedstock metered into the dryer. The feed rate was adjusted as necessary to keep the outlet temperature in a narrow range varying from 70-80 to 80-86.5°C depending upon the run.

The dried powder was collected, sieved through a No. 48 Tyler mesh screen (297 micron diameter openings) and rolled for 30 minutes in a round plastic bottle to eliminate lumps.

The precursors thus obtained were converted to polyimide foams by using a Gerling Moore Batch Cavity Model 4115 microwave oven operating at a frequency of 2450 MHz and a power 5 KW.

The precursor was laid on a substrate, placed in the microwave cavity at room temperature, and exposed to the high frequency radiation for 2 to 12 minutes. The foam thus produced was then further processed (or cured) by heating it at 287.7°C for 15 to 30 minutes in a circulating air oven.

Resiliency, density, and quality of the foam were measured. Resiliency was determined by the ball rebound method described in ASTM Standard D-1564, Suffix B, using a tester fabricated and calibrated by that procedure.

The results of the tests are summarized in Table 1.

The tabulated data demonstrate the importance of the spray drying parameters. For the particular chemical system involved in the tests, for example, spray dryer inlet temperatures of 100-110°C produced superior results.

The data summarized in Table 1 show that a more than three-to-one variation in the density of the polyimide product can be obtained by only moderate variations in the spray dryer outlet temperature. The data furthermore show that, within this range, the outlet temperature has a marked influence on the yield of both the precursor and the final product and on the quality of the latter.

Dryer outlet temperature is particularly important because of its direct influence on the volatiles content of the particulate precursor. Volatiles content increases with decreases in spray dryer outlet temperature and vice versa.

The volatiles content of the particulate precursor is the most important factor in the foaming of the precursor and, therefore, in the properties of the polyimide foam. Precursors with higher volatiles content produce foams with more open and larger cellular structures and lower density. Conversely, those precursors of lower volatiles content produce foams with less open, smaller cells and higher density.

TABLE 1

RUN NO.	INLET °C	OUTLET °C	Δt, °C	AVERAGE FLOW RATE ml/min	POWDER BULK DENSITY g/cc	POWDER BULK DENSITY lbs/ft^3	FOAM PROPERTIES RESILIENCY	FOAM PROPERTIES DENSITY lbs/ft^3	FOAM PROPERTIES DENSITY kg/m^3	FOAM QUALITY
21	110	80-86	30-24	22	0.238	14.9	60-70	1.21	19.4	Poor
22	110	80-74	30-36	54	0.352	22.0	60-70	0.86	13.8	Good
23	110	80-70	30-40	107	0.414	15.8	50-60	0.75	12.0	Good
24	120	80-86.5	40-33.5	335	0.200	12.5	50	1.38	22.1	Poor
25	120	80-75	40-45	80.8	0.368	23.0	50-60	0.67	10.7	Good
26-R	120	80-76	40-44	58.4	0.329	20.5	50	0.66	10.6	Poor
27	130	80-88	50-42	48	0.198	12.4	50-60	1.52	24.3	Poor
28	130	80-77	50-53	83.3	0.241	15.0	50-60	1.06	17.0	Poor
29	130	80-74	50—56	90.4	0.343	21.4	60-70	0.59	9.5	Good
30	100	80-74	20-26	35.8	0.326	20.3	60-70	0.88	14.1	Good
31	100	80-70	20-30	60.9	0.413	25.8	60-70	0.95	15.2	Fair-Good
32	100	80-79	20-21	23.8	0.241	15.0	50	0.88	14.1	Poor

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Density of the polyimide foam is important because most physical properties of a polymeric foam approach a straight-line relationship to density. Among the important properties of which this is true are indentation load deflection and compression set.

Indentation load deflection (ILD) is a measure of the force required to compress a polymeric foam to a specified percentage of its original thickness. ILD is accordingly indicative of the softness or seatability of a foam.

Compression set is the permanent deformation obtained by subjecting a foam to a specified compressive stress (load and time). Compressive set is also indicative of the seatability of a foam and, in addition, is a measure of its durability.

The data in Table 1 show the substantial effect that spray dryer outlet temperature consequently has on ILD and compression set.

The data further show that, when correlated with the spray dryer or reactor inlet temperature, spray dryer outlet temperature can be so controlled as to simultaneously optimize yield and foam quality and produce optimum cellular structure.

To further demonstrate that spray dryer outlet temperature is consequential, that variations in that parameter can be utilized to control the properties of the polyimide product into which the precursor is converted, and that our process is equally useful in making precursors for other polyimides, terpolymers of the character identified above were prepared by forming the methyl half ester of 3,3', 4,4'-benzophenonetetracarboxylic acid in the manner described above. The half ester solution was cooled to 25-35°C (77-95°F) and 2,6 diaminopyridine (32.8 g, 0.3 mole and p-p'-methylene dianiline (99.1 g, 0.5 mole) were added and the contents of the flask mixed for 15 minutes. 1,6 Diaminohexane (23.7 g, 0.2 mole) was then added at a slow enough rate to keep the reaction temperature from exceeding 65°C (149°F).

PD-40

FS-C surfactant (0.1 weight percent) was added to the mixture, the latter diluted with 30 phr of methyl alcohol, and the resulting liquid resin feedstock spray dried in the same reactor operated at an inlet temperature of 100°C and outlet temperatures in the range of 58-63 to 75-80°F. The outlet temperature was again controlled by regulating the rate-of-flow of the feedstock through the reactor or spray dryer.

The dry powder was processed and converted to a polyimide foam as described above, and various parameters which this test was designed to characterize were measured. The results of this series of tests are tabulated in the following table (Table 2).

TABLE 2

FOAM NO.	INLET TEMPERATURE (°C)	OUTLET TEMPERATURE (°C)	POWDER YIELD kg/h	POWDER YIELD lbs/h	POWDER PRECURSOR VOLATILE CONTENT	FOAM YIELD ROUGH CUT	DENSITY kg/m^3	DENSITY lbs/ft^3	TYPE OF FOAM
45-62	100	58-63	wet powder		-	10	7.2	0.45	Excessive Reticulation
68-78	100	63-67	2.9	6.4	21.4	82	10.2	0.64	Good. Moderate Reticulation
77-87	100	67-70	2.3	5.0	20.7	65	20.0	1.25	Good. Some Reticulation
70-80	100	70-75	1.7	3.8	19.2	47	22.2	1.39	Fair. Striations present
46-63	100	75-80	0.64	1.4	19.0	35	25.6	1.60	Poor. Full of voids

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The effect of dryer outlet temperature on yield of precursor and terpolyimide foam, on foam density, and on the character of the foam are all noteworthy.

The foregoing, and other series of tests, also demonstrated that atomizer speed is an important parameter in the practice of our invention, that it has a pronounced effect on particle size, and that precursor particle size has a marked effect on the properties of the polyimide foam into which it is converted.

One set of tests in which this was demonstrated involved spray dryer system 20 and a liquid terpolyimide resin containing 3,3', 4,4'-benzophenonetetracarboxylic acid methyl ester, 2,6-diamino pyridine, p,p'-methylene dianiline, and 1,3-diamino propane in a mole ratio of 1.0: 0.3: 0.6: 0.1 with a 30 phr dilution ration of methanol.

Atomizer speeds below 30,000 rpm proved unsatisfactory because of incomplete atomization of the liquid resin and consequent generation of a wet powder.

Speeds of 37,000 and 40,000 rpm similarly proved unsatisfactory. This produced procursors with small particle sizes, and these yielded polyimide foams with flaws and unwanted, rigid, cellular structures.

Atomizer speeds in the range of 32,000-35,000 rpm followed by screening through a 24 Tyler mesh screen produced precursors which could be converted into high quality foams with good mechanical properties.

These tests also demonstrated that grinding to reduce the size of large particles can prove unsatisfactory because of the large proportion of fines this generates.

Exemplary particle size distributions obtained in the tests under discussion are shown in Figure 3. Curve 60 shows that operation of the atomizer in the preferred 32,000-35,000 rpm range produced an optimum particle size distribution. Curves 62 and 64 show that precursors prepared by operating the atomizer at a slower speed and by employing grinding had much less useful particle size distributions.

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Other results of exemplary tests in the series just described are tabulated below.

TABLE 3

Maximum Particle Size	Indentation Load Deflection				Foam Quality
	25%		65%		
Tyler Mesh (microns)	N	(lbf)	N	(lbf)	
#24 (707)	138	39	534	120	Good Cellular Structure
#48 (297)	245	55	1076	242	Rigid Structure
Pulverized (<297 microns)	267	60	1054	237	Rigid Structure large flaws

The tabulated data make it clear that, by virtue of its effect on the particle size of the precursor, the operating speed of the atomizer has a marked effect on indentation load deflection as well as the quality of the polyimide foam.

The foams identified in Table 3 were produced by foaming and curing the precursor on TEFLON® coated glass (type 7267/114) in a 15KW microwave oven using a powder loading of 15KG (33 pounds) at a thickness of 6.35 cm (2.5 inches).

The "pulverized" precursor was produced in a Pulvette bench model grinder.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therfore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description; and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

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What is claimed is:

1. A method of preparing a dry, foamable, particulate precursor which can be converted into a polyimide by heating it, said method comprising the steps of: forming a primary diamine, 3,3', 4,4'-benzophenone-tetracarboxylic acid ester solution by dissolving one or more such diamines and the aforesaid acid or an anhydride thereof in a lower alkyl alcohol, atomizing said solution, and drying the droplets obtained by atomizing the diamine, ester solution with a heated gas.

2. A method of preparing a polyimide precursor as defined in Claim 1 in which the atomized droplets of diamine, ester solution are dried in a chamber having an inlet and an outlet for a heated gas and in which the inlet temperature of said gas is maintained in the range of 100-110°C and the outlet temperature thereof is limited to a maximum of 80°C.

3. A method of preparing a polyimide precursor as defined in Claim 1 wherein the outlet temperature of said gas is controlled by regulating the rate of feed of the diamine, ester solution to the chamber in which it is dried.

4. A method of preparing a polyimide precursor as defined in Claim 1 wherein the gas with which the atomized droplets of the diamine, ester solution are dried is introduced into said chamber around, and in entraining relationship with, said droplets.

5. A method of preparing a polyimide precursor as defined in Claim 1 wherein said diamine, ester solution is diluted with from 20 to 30 parts of alkyl alcohol per 100 parts of solution prior to atomizing said solution.

6. A method of preparing a polyimide precursor as defined in Claim 1 wherein atomization of the diamine,

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ester solution is effected with a rotary type atomizer and wherein the atomizer is operated at a speed in the range of 32,000 to 35,000 rpm.

7. A method of preparing a polyimide precursor as defined in Claim 1 wherein the dried particulate material is screened through a 24-48 mesh (Tyler) screen to generate a lump-free powder of sufficiently large particle size to be processable into a polyimide foam with a relatively homogeneous cellular structure.

8. A method of preparing a polyimide which includes the steps of making a precursor by a process as defined in Claim 1, Claim 2 or Claim 3, and converting the precursor to a polyimide by the application of heat.

9. A method of preparing a polyimide which includes the steps of:

forming a half ester of 3,3', 4,4'-benzophenone-tetracarboxylic acid by reacting said acid or an anhydride thereof with a lower alkyl alcohol;

dissolving one or more primary diamines in the half ester, alcohol solution;

spray drying the material thus formed to convert it into a dry particulate polyimide precursor; and

converting the precursor to a polyimide by heating it.

10. A method of preparing a polyimide as defined in Claim 9 in which the diamine, ester solution also includes a surface active agent in an amount ranging from 0.01 to 1 percent based on the weight of the ester and diamine or diamines.

11. A method of preparing a polyimide as defined in Claim 9 wherein the 3,3', 4,4'-benzophenonetetracarboxylic acid ester and the diamine constituent are present in

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said diamine, ester solution in amounts such that the imide forming functionalities are substantially equimolar.

12. A method of preparing a polyimide as defined in Claim 9 in which the diamine, ester solution contains a plurality of diamines, one of said diamines being heterocyclic and having nitrogen in the ring, another of said diamines being a para- or meta-substituted aromatic diamine which is free of aliphatic moieties, and any additional diamine being either a heterocyclic or an aromatic diamine as aforesaid.

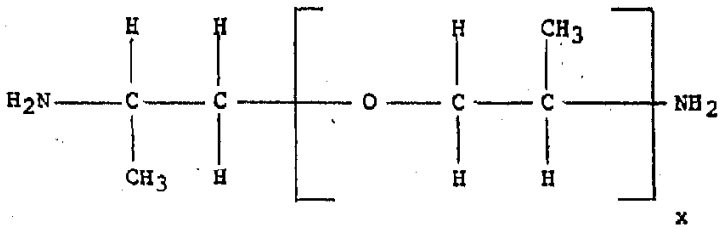
13. A method of preparing a polyimide as defined in Claim 12 wherein said heterocyclic diamine is present in said solution in a ratio of 0.4 to 0.6 mole of diamine per mole of 3,3', 4,4'-benzophenonetetracarboxylic acid ester.

14. A method of preparing a polyimide as defined in Claim 9 wherein the diamine, ester solution contains at least three diamines, one of said diamines being heterocyclic and having nitrogen in the ring, another of said diamines being a para- or meta-substituted aromatic diamine which is free of aliphatic moieties, and a third of said diamines being aliphatic.

15. A method of preparing a polyimide as defined in Claim 14 in which the diamine, ester solution contains from 0.05 to 0.3 mole of aliphatic diamine and from 0.1 to 0.3 mole of heterocyclic diamine per mole of 3,3', 4'4-benzophenonetetracarboxylic acid ester.

16. A method of preparing a polyimide as defined in Claim 14 wherein the aliphatic diamine in the diamine solution has from three to twelve carbon atoms.

17. A method of preparing a polyimide as defined in Claim 14 wherein the aliphatic diamine in the diamine, ester solution has the formula



where x is on the order of 2.6.

18. A method of preparing a polyimide as defined in either of the preceding Claims 12 or 14 wherein the heterocyclic and aromatic diamines are selected from the group consisting of:

2,6-diaminopyridine
3,5-diaminopyridine
3,3'-diaminodiphenyl sulfone
4,4'-diaminodiphenyl sulfone
4,4'-diaminodiphenyl sulfide
3,3'-diaminodiphenyl ether
4,4'-diaminodiphenyl ether
meta-phenylene diamine
para-phenylene diamine
p,p'-methylene dianiline
2,6-diamino toluene
2,4-diamino toluene

19. A method of preparing a polyimide which includes the steps of making a precursor by a process as defined in Claim 4 or Claim 5 and converting the precursor to a polyimide by the application of heat.

20. A method of preparing a polyimide which includes the steps of making a precursor by a process as defined in Claim 6 or Claim 7 and converting the precursor to a polyimide by the application of heat.

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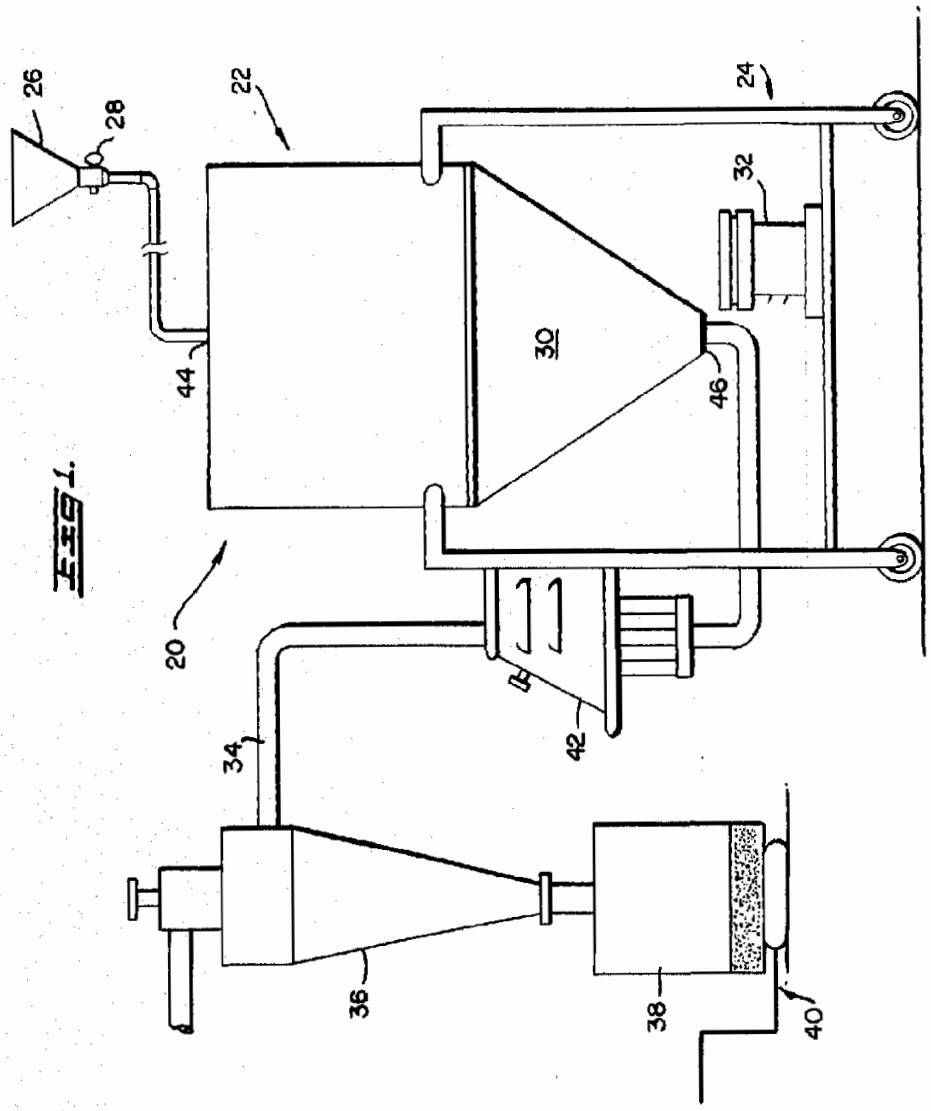


FIG 1.

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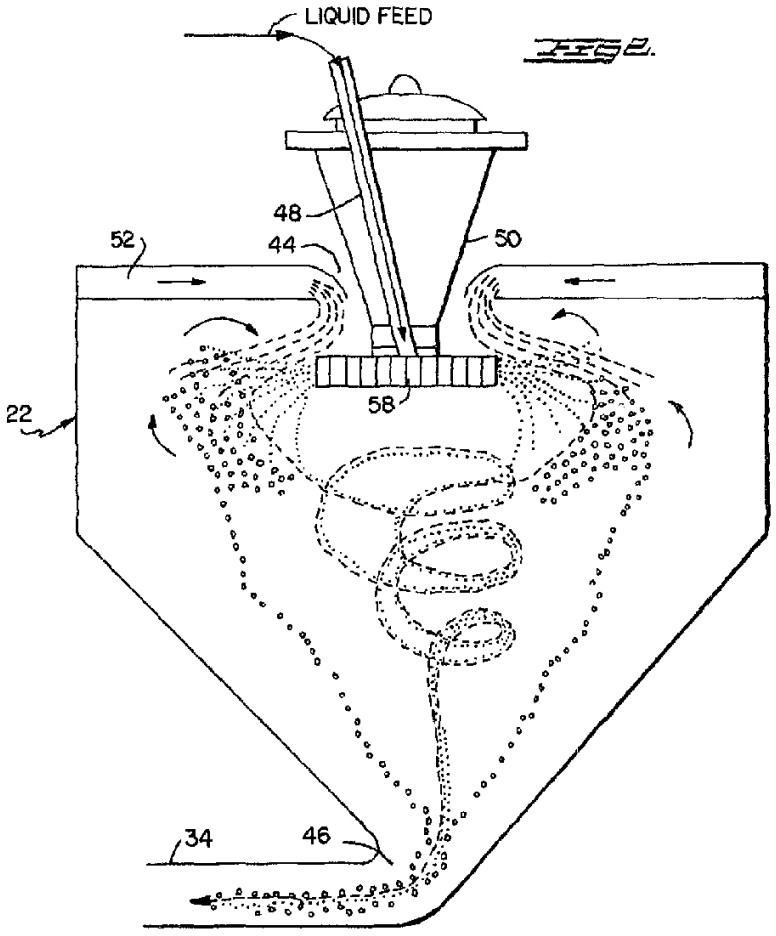


Fig 2.

LEGEND

..... POWDER
– – – – DRYING AIR
..... LIQUID DROPLETS
——— LIQUID RESIN

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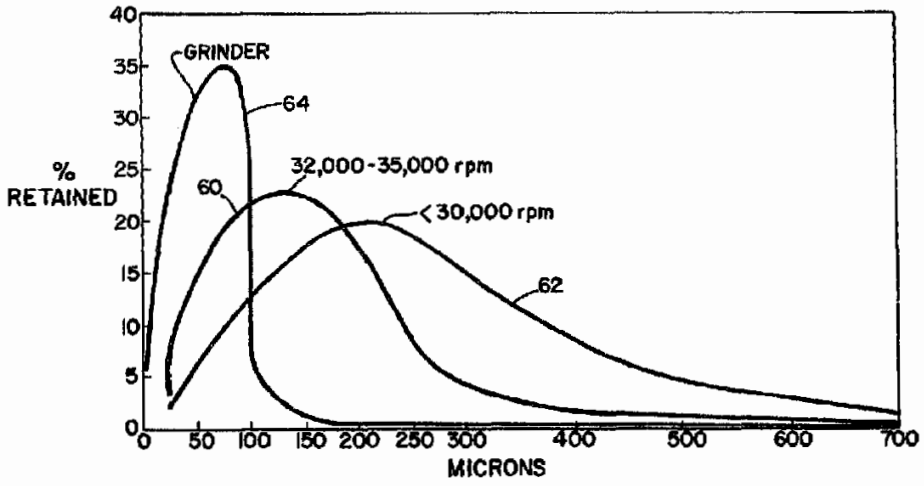


Fig.3

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(19)(CA) **CANADIAN PATENT** (12)

(54) Cholesterol Free Butter Flavored Granules with Low Caloric Content

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(30) (US) U.S.A. 89,683 1987/08/26

(57) 18 Claims

NO DRAWING

Canada

CCA 3254 (10-89) 41

5,385,603

87-364

BUTTER FLAVORED GRANULES

ABSTRACT OF THE DISCLOSURE

Granules having natural butter flavor are provided, the granules being formed of a carrier such as maltodextrin, a small amount of a fat such as a vegetable oil, and enzyme modified butter oil, with or without, but preferably with a water soluble butter flavor component. The granules may include salt to taste, if desired and may also include an emulsifier. The granules of the invention are very low in calories, have a high intensity butter flavor, have no cholesterol and dissolve instantly upon contact with wet and hot foods to provide the flavor and mouthfeel of butter.

BACKGROUND OF THE INVENTION

Butter is a very popular food made of butter fat or cream, milk solids, and natural coloring, and may also contain salt. The fat content of butter is usually about 80%.

Although butter is very high in cholesterol, containing about 220mg cholesterol/100g, and very high in calories, more than 700 calories/100g, butter is nevertheless an extremely popular product. The popularity of butter is mainly due to its unique and characteristic flavor which is the basis for its wide acceptance and utilization as an ingredient in food products. Health experts have recommended the elimination from or reduction of butter in the diet in order to reduce and control the ingestion of cholesterol. This is due to high cholesterol diets having been associated with increased incidence in heart disease.

Physicians have also recommended the elimination or reduction of butter from the diet because of the high caloric content.

The art has recognized the need for a product having the typical and characteristic flavor of butter but without the cholesterol and the high caloric content of butter. U.S. Patent No. 3,653,921 of Buhler, et al. describes a method for preparing a butter flavor composition consisting of lipolyzed butter oil. The product of this patent provides a highly effective substitute for the flavor of butter. However, the product is best used by first mixing with hot water prior to use.

In U.S. Patent No. 4,414,229, Bakal, et al. describe a process for the preparation of a spread having natural butter flavor. The butter flavor spread of this patent provides highly effective butter flavor in the form of a spread and is substantially free of cholesterol but does provide a higher caloric con-

tent than does the butter flavor composition of U.S. Patent No. 3,653,921.

SUMMARY OF THE INVENTION

It is accordingly a primary object of the present invention to provide a composition which can easily be used without first being mixed with water and which provides both natural butter flavor and the mouthfeel of butter without the high cholesterol and high caloric content of butter.

It is yet another object of the present invention to provide butter flavored granules which can be simply sprinkled on hot, moist foods to provide natural butter flavor without cholesterol and with very little caloric content.

It is yet a further object of the present invention to provide a method of producing the butter flavored granules.

Other objects and advantages of the present invention will be apparent from a further reading of the specification and of the appended claims.

With the above and other objects in view, the present invention mainly comprises a granulated product formed of a small amount of fat, maltodextrin having a low DE (dextrose equivalent), the DE being less than 5, a butter flavor component consisting at least of an oil soluble component and preferably also including a water soluble component, and an inert carrier which may be maltodextrin of a higher DE. The product may also include salt to taste.

In accordance with a preferred embodiment of the inven-

tion, the amount of fat is between 1 and 20% by weight of the composition, preferably 5-20% by weight. The fat is most preferably a vegetable oil.

The amount of salt is preferably between about 1-10% by weight.

The amount of low DE maltodextrin is preferably between about 1-10% by weight, the DE thereof being preferably less than 5. Most preferably this maltodextrin is derived from potato.

The butter flavor component, which as indicated above consists at least of an oil soluble component and preferably also includes a water soluble component, is preferably present in an amount of about 0.05-10% by weight, most preferably between about 1-5% by weight. All percentages by weight are of the final product on a dry solids basis.

The oil soluble component of the butter flavor component may be an enzyme modified butter oil (EMBO) or lipolyzed butter oil (LBO).

EMBO or LBO is obtained by incubating either milk fat, derived directly from whole milk, or butter oil derived from butter with a lipase (esterase) enzyme as described, for example, in U.S. Patent No. 2,794,743. During the incubation period the enzyme system catalytically releases fatty acids from the butter fat and results in certain end products. Specific action of the lipase system releases volatile, flavorful, fatty acids including butyric, caproic, caprylic and capric acids in much greater molar concentrations than, but together with, long chain fatty acids. To control the flavor development in the finished product, the system is heated to completely destroy the enzyme activity and to reduce the bacterial counts to very low levels.

The water soluble component consists of distillates from butter or cultured milk. This product, also known as starter distillate, is the mixture of flavor compounds distilled from butter or cultured milk. It contains the flavor compounds which are volatile with water at 212°F. While the major component of starter distillate is diacetyl, the starter distillate as a whole, however, gives a flavor which is much more pleasant than that of synthetic diacetyl because of the presence of other flavor substances produced by the bacteria used in culturing the milk. Starter distillate is obtainable commercially as "starter distillate".

The water soluble butter flavor component is used in the composition of the present invention in an amount of up to 1% by weight of the final product, and preferably in an amount of 0.05-0.5% of the final product on the dry solids basis.

The above mentioned components are mixed with an inert carrier such as dextrins, whey solids, corn syrup solids and the like. The most preferred inert carrier is maltodextrin, namely maltodextrins with a DE of between 10 and 20.

The preferred ranges of components of the compositions of the present invention are set forth below:

	Percent By Weight
Low DE potato maltodextrin (less than 5 DE)	1-10; pref. 2-8
Vegetable oil	1-20; pref. 5-10
Salt	0-10; pref. 1-3
EMBO	0.5-10; pref. 1-5
Water soluble butter flavor component (starter distillate)	0.0-1.0; pref. 0.05-0.5
Emulsifier (lecithin)	0-1.0; pref. 0.01-0.05
Maltodextrin (10 DE-20 DE)	q.s. 100%

The preferred process for making the product of the invention consists in first preparing a 50-60% solids emulsion, heating the emulsion to between about 120-160°F, and passing the emulsion through a homogenizer to form a stable emulsion. This emulsion is then conveyed to a spray tower equipped with pressure nozzles and with the provision for the introduction of an inert gas such as nitrogen or carbon dioxide (preferably carbon dioxide). The emulsion is then sprayed by means of the inert gas at an exit air temperature at the spray tower of preferably about 210°F and utilizing a carbon dioxide pressure of 15 psig.

The resulting dry product has a bulk density of between 20 and 35g/100cc and preferably between 22 and 30g/100cc. The final product exhibits the following characteristics:

1. It has only 4 calories/gram yet has the flavor intensity of about 10g of butter, for over 94% savings in calories.
2. It has no cholesterol.
3. It has the natural flavor of butter.
4. It dissolves instantly upon contact with wet and hot foods, thus providing not only the flavor but also the mouthfeel of butter.
5. It has an extended shelf-life and is extremely stable to oxidation.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are given to further illustrate the present invention. The scope of the invention is not, however, meant to be limited to the specific details of the examples.

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EXAMPLE 1

A mixture of 5% (all percentages are by weight) of maltodextrin from potato having a DE of 3, 5% vegetable oil, 2% salt, 4% EMBO, 1% starter distillate, 0.5% lecithin and 82.5% maltodextrin having a DE of 10 is emulsified with water of equal amount and the emulsion is heated to a temperature of about 140°F. The emulsion is passed through a homogenizer to form a stable emulsion which is then conveyed to a spray tower equipped with pressure nozzles. The resulting emulsion is spray dried under a carbon dioxide pressure of 15 psig at a temperature of about 210°F.

The resulting dry product has a bulk density of about 25g/cc. The product has a caloric content of about 4 calories per gram, each gram having the flavor intensity of about 10g of butter. The butter flavor is natural butter flavor and all components of the granular product are natural.

The granules may be sprinkled on a hot, wet food such as cooked string beans, cooked potatos, etc. to provide both the flavor and mouthfeel of butter.

The product has a long shelf-life. The product is extremely stable to oxidation.

EXAMPLE 2

Example 1 is repeated, however utilizing the components in the following percentages: 4% maltodextrin DE 1, 6% vegetable oil, 1% salt, 3% EMBO, 0.5% starter distillate, 0.5% lecithin, and 85% maltodextrin 10 DE.

The resulting product has substantially the same characteristics as the product of Example 1.

While the invention has been illustrated with respect to particular compositions, it is apparent that various modifications of the invention can be made without departing from the spirit or scope thereof.

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The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. Butter flavored granules having a natural butter flavor and the mouthfeel of butter without providing the cholesterol and calories of butter, said granules being formed by spray drying under pressure at a temperature of about 210°F an emulsion of a natural butter flavor component consisting essentially of an oil soluble component formed of an enzyme modified butter oil or lipolyzed butter oil and being present in an amount of about 0.05-10% by weight of the granules, a fat in an amount of about 1-20% by weight of the granules, and maltodextrin having a low dextrose equivalent of less than 5, in an amount of about 1-10% by weight of the granules, all distributed in a balance of an inert carrier selected from the group consisting of dextrins, maltodextrins, whey solids and corn syrup solids.

2. Butter flavored granules according to claim 1, wherein said inert carrier is a maltodextrin having a dextrose equivalent of between about 10 and 20.

3. Butter flavored granules according to claim 1, wherein said butter flavor component includes starter distillate in an amount of up to 1% by weight as water soluble component.

4. Butter flavored granules according to claim 3, wherein said inert carrier is a maltodextrin having a dextrose equivalent of between about 10 and 20.

5. Butter flavored granules according to claim 4, wherein said fat is a vegetable oil.

6. Butter flavored granules according to claim 5 and also including salt.

7. Butter flavored granules according to claim 6 and also including an emulsifier.

8. Butter flavored granules according to claim 6, wherein said salt is present in an amount of up to about 10% by weight.

9. Butter flavored granules according to claim 8 and including an emulsifier in an amount of up to 1% by weight.

10. Butter flavored granules having a natural butter flavor and the mouthfeel of butter without providing the cholesterol and calories of butter, said granules being formed of a natural butter flavor component consisting essentially of an oil soluble component formed of an enzyme modified butter oil or a lipolyzed butter oil in an amount of about 0.05-10% by weight, a fat in an amount of about 1-20% by weight and maltodextrin having a low dextrose equivalent of less than 5 in an amount of about 1-10% by weight, all distributed in a balance of an inert carrier selected from the group consisting of dextrins, maltodextrins, whey solids and corn syrup solids.

11. Butter flavored granules according to claim 10, wherein said butter flavor component includes starter

distillate in an amount of up to 1% by weight as water soluble component.

12. Method of producing butter flavored granules having a natural butter flavor and the mouthfeel of butter without providing the cholesterol and calories of butter, which comprises forming a 50-60% solids emulsion of a natural butter flavor component consisting essentially of an oil soluble component formed of an enzyme modified butter oil or lipolyzed butter oil and being present in an amount of about 0.05-10% by weight, a fat in an amount of about 1-20% by weight and maltodextrin having a low dextrose equivalent of less than 5, in an amount of about 1-10% by weight, all distributed in a balance of an inert carrier, heating the emulsion to between about 120°-160°F, homogenizing the emulsion and spray drying the formed emulsion under pressure of an inert gas and at a temperature of about 210°F.

13. Method according to claim 12, wherein said inert carrier is a maltodextrin.

14. Method according to claim 12, wherein the emulsion includes an emulsifier.

15. Method according to claim 12, wherein the emulsion includes salt in an amount of up to about 10% by weight.

16. Method of producing butter flavored granules having a natural butter flavor and the mouthfeel of butter without providing the cholesterol and calories of butter, which comprises forming a 50-60% solids emulsion of a natural

butter flavor component consisting essentially of an oil soluble component formed of an enzyme modified butter oil or lipolyzed butter oil and being present in an amount of about 0.05-10% by weight, a fat in an amount of about 1-20% by weight and maltodextrin having a low dextrose equivalent of less than 5, in an amount of about 1-10% by weight, all distributed in a balance of an inert carrier selected from the group consisting of dextrins, maltodextrins, whey solids and corn syrup solids, heating the emulsion to between about 120°-160°F, homogenizing the emulsion and spray drying the formed emulsion under pressure of an inert gas and at a temperature of about 210°F.

17. Method according to claim 16, wherein the emulsion includes an emulsifier in an amount to 1% by weight.

18. Method according to claim 16, wherein said butter flavor component includes starter distillate in an amount up to 1% by weight.

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SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente

OPIC
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Ottawa Hull K1A 0C9

(11) (C) **1,334,460**

(21) 593,125

(22) 1989/03/08

(45) 1995/02/14

(52) 402-6

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Trade marks
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Industrial design
Integrated circuit topography

(51) Intl.Cl.[5] B01D-001/16; C08J-003/16; C08L-033/00

(19)(CA) **CANADIAN PATENT** (12)

(54) Method for Spray-Drying Polymer Emulsions

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Arndt, Peter J. , Germany (Federal Republic of)

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(57) 10 Claims

NO DRAWING

Consommation et Affaires commerciales Canada
Consumer and Corporate Affairs Canada

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ABSTRACT OF THE DISCLOSURE

The formation of interfering polymer deposits in spray drying apparatus during the spray drying of aqueous dispersions or solutions of polymers in a stream of warm air is avoided if water is atomized together with the dispersion or solution.

The present invention relates to a method for making spray dried polymer powders by atomizing an aqueous dispersion or solution of a polymer in a warm air stream and separating the polymer powder from the warm air stream.

It is known to prepare powdered emulsion polymers by the spray drying of aqueous polymer dispersions. In this, a careful control of temperature in the spraying tower has proved advantageous for preparing unglazed polymer powders or powders from dispersions having low minimum film forming temperatures (MFT).

DE-C 25 12 238 (granted 13 Jan. 1977) describes the preparation of a powdered acrylic resin having a high content of carboxyl groups by the spray drying of an aqueous dispersion. It is there indicated as essential to not exceed the MFT in the spray drying process.

Aqueous polymer dispersions with high solids contents of, for example, 40 to 60 percent by weight are sensitive systems which tend to form deposits and coagulates at elevated temperatures or under the influence of shearing forces. This is particularly true for dispersions having a low MFT, for example under 60°C, and for dispersions of emulsion polymers having a low dynamic glass transition temperature ($T\lambda_{max}$). Because of this sensitivity, considerable difficulties are often encountered in the spray drying of aqueous polymer dispersions. When flowing onto the rapidly rotating atomizer disk, the dispersion is heated by frictional forces and is subjected to strong shearing forces. Deposits in the liquid distributor and on the atomization disk of the spray drying apparatus are the result.

IFF000659666

Similar difficulties occur during the spray drying of aqueous polymer solutions.

The problem to be solved by the invention is to avoid the aforementioned difficulties in the atomization of aqueous dispersions and solutions, particularly in the spray drying of temperature sensitive and shear sensitive dispersions having an MFT below 60°C and a dynamic glass transition temperature of the emulsion polymer below 150°C.

It has been found that if water is atomized together with the dispersion or solution, polymer deposits in the liquid distributor and in the atomization apparatus are prevented. This is not brought about by any dilution effect, since the addition of water to the dispersion or the solution itself has no corresponding effect. Rather, it can more likely be assumed that the water acts as a coolant and discourages temperature dependent coagulation and deposition processes. To the extent that small amounts of deposits may nevertheless arise, they can be more readily removed than when they are formed in the absence of added water.

The invention in a broad aspect provides a method for making a spray dried polymer powder, which method comprises atomizing water and an aqueous dispersion or solution of a polymer in a warm air stream, the amount of water atomized per unit time being smaller than the amount of dispersion or solution, and separating the polymer powder from the warm air stream.

The dispersion or solution is atomized in a technical spray drying apparatus preferably by means of a rapidly rotating

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disk. The preferred disk velocity is mostly in the range from 5000 to 25000 revolutions per minute (rpm). It is suitable to let the dispersion or solution and the water flow simultaneously, but separately, onto the rapidly rotating disk. For this purpose, an atomization apparatus is suitably outfitted with one or more supplementary supply lines such that one or more outlet openings in the liquid distributor are located directly over the atomizer disk and the water can flow directly over the atomizer disk

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directly, but separately from the dispersion or solution.

The amount of water added per unit time is, as a rule, smaller than the amount of dispersion or solution atomized in the same time period, for example 1 to 20 percent by weight thereof. Preferably, 2.5 to 7.5 percent of water, in each case based on the amount of dispersion or solution, are used. The effect of the water is generally not adversely affected if it contains limited amount of dissolved or dispersed materials, so long as they do not noticeably increase viscosity or do not bring about undesired interactions with the dispersion or solution. Possible contents are, for example, surfactants and non-volatile additives which serve to modify the polymer powder.

In a drying tower, the air stream is conventionally led in cocurrent with the dispersion or solution sprayed thereinto, i.e. from top to bottom through the drying tower. The air stream is conducted from the exit of the drying tower into one or more cyclone separators where the dried polymer powder is separated. The powder contains at most a residual moisture between 1 and 5 percent by weight.

The air introduced into the drying tower as a rule has a temperature in the region from 50°C to 200°C, preferably from 60°C to 120°C. The air temperature, as a result of the energy absorbed in the evaporation of the water, decreases from top to bottom and the air exits at 30°C to 100°C, preferably at 30°C to 50°C. The difference between the entry and exit temperatures (T_E/T_A) depends on the relative amounts of air and atomized dispersion and can be controlled through this relationship.

According to a preferred embodiment of the invention, the dispersion is dried at an entry temperature T_E below the dynamic

glass transition temperature but above the MFT and at an exit temperature T_A below 65°C but above the MFT. It is further preferred that the amount of dry air introduced in the spray drying is so adjusted with respect to the amount of sprayed dispersion that the difference between the entry and exit temperatures (T_E - T_A) does not exceed 65°C.

If dispersions are used in the process of the invention, then they should suitably have as high a solids content as possible. This can lie between 10 and 60, preferably between 20 and 50, percent by weight. In order to be able to spray the dispersion into fine droplets, its viscosity should not be above 4000 mPa.s. A viscosity below 1000, and particularly below 100, mPa.s is advantageous.

As a rule, the dispersion contains an anionic emulsifier, for example in a concentration of 0.03 to 3 percent by weight of the aqueous phase. In addition thereto, nonionic emulsifiers may be present, for example up to 5 percent by weight, and these may also be present as the sole emulsifier.

The dispersions used for spray drying can be prepared according to known methods. Although the invention can be used to advantage with every dispersion of a spray dryable emulsion polymer, because of the increased energy demand corresponding to the amount of water added it will in practice be used only in those cases in which the dispersion without water addition can only by spray dried with difficulty or not at all.

Among the difficultly sprayable dispersions which can be processed with particular advantage according to the method of the invention are such whose minimum film forming temperature (MFT) is at least 50°C below the dynamic glass transition

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temperature, and particularly those whose MFT is below 60°C. The dynamic glass transition temperature ($T_{\lambda\ -max}$) is preferably below 150°C.

A group of dispersions to which the aforementioned criteria as a rule pertain include emulsion polymers comprising 20 to 70 percent by weight of units of acrylic acid or of methacrylic acid, 40 to 80 percent by weight of units of lower alkyl esters of acrylic acid and/or methacrylic acid or mixtures thereof with styrene, as well as up to 10 percent by weight of units of other unsaturated free radically copolymerizable comonomers.

Aqueous solution of water soluble polymers can also advantageously be spray dried according to the method of the invention. Typical polymers of this kind comprise at least 50 percent by weight of acrylic acid or methacrylic acid or the water soluble salts thereof, any balance comprising other monomers copolymerizable therewith, such as acrylamide, methacrylamide, acrylonitrile or methacrylonitrile, and alkyl esters or hydroxyalkyl esters of acrylic acid or of methacrylic acid. The lower limit of the content of acrylic acid or of methacrylic acid is set only by the water solubility.

Aqueous polymer solutions are sprayable if their viscosity is not above 2000 mPa.s, and is preferably below 500 mPa.s. The solution viscosity is dependent on molecular weight and on solids content, and also on the salt content for polyelectrolytes. Solutions of polyacrylic acid having a molecular weight below 2000 can only be spray dried at solids contents up to 50 percent by weight, whereas at a molecular weight of 50,000 only concentrations up to 30 percent by weight are still workable.

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The spray dried polymer powder as a rule consists of powder grains of an average size of about 50 microns (μ). In a microphotograph, the grains at 100x appear sharply defined and translucent to transparent, which suggests a more or less strong glazing or melting of the latex particles.

The polymer powders are, for example, suitable for the preparation of medicament coatings or as thickening agents for aqueous alkali media.

A better understanding of the present invention and of its many advantages will be had by referring to the following specific examples, given by way of illustration.

EXAMPLES

Example 1

An aqueous synthetic resin dispersion having a solids content of 30 percent by weight which contains a dispersed copolymer formed from 50 percent by weight of ethyl acrylate and 50 percent by weight of methacrylic acid having an average particle size of 100 nanometers, and 2.4 percent of an anionic emulsifier ("HOSTAPAL*BV", conc., Hoechst AG), and adjusted to pH 2.6 was used for spray drying. The dispersion had a viscosity of 6 mPa.s, a minimum film forming temperature of 28°C, and a white point of 17°C. The dispersed copolymer had a dynamic glass transition temperature ($T\lambda_{max}$) of 134°C and a shear modulus of 1650 N/mm^2 at 20°C.

For spray drying, a spray tower was employed which had at its head an atomization disk rotating at 10,000 rpm and through which heated air at 80°C to 90°C was passed from top to

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bottom at 18000 m³/hour in cocurrent with the material sprayed. 190 kg/hour of the aqueous dispersion was lead onto the

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atomization disk by way of a tubular conduit at the head of the spray tower. By way of a second tubular conduit, 8 - 10 kg/hour of water were led to the atomization disk at the same time. At the foot of the tower, the dried copolymer was separated from the air stream at a temperature of 40°C - 50°C in the form of a finely divided powder.

If the dispersion is diluted with the same amount of water, or if the water is omitted altogether, then deposits form on the atomizer disk after a short period of operation, which deposits heat up and char because of rubbing against the stationary parts of the atomization mechanism so that the product is contaminated with charred particles.

Example 2

An aqueous solution of a copolymer formed of 85 percent by weight of acrylic acid and 15 percent by weight of ethyl acrylate, having a weight average molecular weight of 1700 to 2000, a solids content of 49 percent by weight, a pH value of 1.5, and a viscosity of 210 mPa.s, is used for spray drying.

A spray drying apparatus was used which had an atomizer disk rotating at 20,000 rpm and through which air heated at 65°C - 70°C was led from top to bottom at 1000 m^3/hour in cocurrent with the material sprayed. The exit temperature of the air was 40°C - 45°C.

By way of separate tubular conduits, 120 kg of the solution and 3 - 4 kg of water per hour were flowed onto the atomization disk. At the foot of the apparatus, a fine white polymer powder was obtained. If the solution was diluted with the same amount of water or if the added water was omitted entirely, disturbances of the kind described in Example 1 arose after a short time.

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Example 3

The procedure of Example 2 was followed, but 100 kg/h of an aqueous solution of sodium polyacrylate (molecular weight 1700 - 2000) having a pH value of 7.5 and a viscosity of 133 mPa.s were used under otherwise equal conditions. The result corresponded with that of the previous Example.

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WHAT IS CLAIMED IS:

1. A method for making a spray dried polymer powder, which method comprises atomizing water and an aqueous dispersion or solution of a polymer in a warm air stream, the amount of water atomized per unit time being smaller than the amount of dispersion or solution, and separating the polymer powder from the warm air stream.

2. A method as defined in claim 1 wherein the dispersion or solution and the water are atomized by means of a rapidly rotating disk.

3. A method as defined in claim 2 wherein the dispersion or solution and the water are concurrently, but separately, flowed onto the rapidly rotating disk.

4. A method as defined in claim 1 wherein said dispersion is a film forming dispersion having a minimum film forming temperature below 60°C.

5. A method as defined in claim 4 wherein said polymer is an emulsion polymer having a dynamic glass transition temperature, $T_{\lambda-max}$ below 150°C.

6. A method as defined in claim 1 wherein said aqueous dispersion is a dispersion of a polymer comprising 20 to 70 percent by weight of a member selected from the group consisting of acrylic acid, methacrylic acid, and the water soluble salts of these acids; 40 to 80 percent by weight of a member selected from the group consisting of lower alkyl esters of acrylic acid, lower alkyl esters of methacrylic acid, and mixtures of such esters with styrene; and up to 10 percent by weight of further,

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different, unsaturated, free radically polymerizable comonomers.

7. A method as defined in claim 1 wherein said dispersion has a minimum film forming temperature which is at least 50°C below the dynamic glass transition temperature of the polymer therein.

8. A method as defined in claim 4 wherein said dispersion is dried by spray drying with warm air having an entry temperature below the dynamic glass transition temperature but above the minimum film forming temperature of the polymer in said dispersion and at an exit temperature below 65°C, but above the minimum film forming temperature of said polymer.

9. A method as defined in claim 1 wherein said aqueous solution is a solution of a polymer comprising at least 50 percent by weight of a member selected from the group consisting of acrylic acid, methacrylic acid, and the water soluble salts of these acids, the balance being other monomers copolymerizable therewith.

10. A method as defined in claim 1 wherein the amount of warm air introduced in spray drying is so adjusted with respect to the dispersion or solution sprayed that the temperature difference between the entry temperature and the exit temperature of the air is not greater than 65°C.

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(54) Titre : PROCEDE DE FABRICATION DE PRODUITS AMORPHES PAR SECHAGE PAR CONVECTION

(54) Title: PROCESS FOR THE MANUFACTURE OF AMORPHOUS PRODUCTS BY MEANS OF CONVECTION DRYING

(57) Abrégé/Abstract:
The invention relates to a rapid and readily reproducible process for producing dry, amorphous products which, besides biologically active, in particular therapeutically active, material, contain substance mixtures for stabilization by means of convection drying. The invention also relates to the amorphous, microscopically homogeneous products which are obtained by this process, are in the form of powders and have a uniform geometric, in particular spherical, shape. The invention furthermore relates to the use of substance mixtures for stabilizing biologically active material, in particular proteins by means of spray drying.

Abstract

The invention relates to a rapid and readily reproducible process for producing dry, amorphous products which, besides biologically active, in particular therapeutically active, material, contain substance mixtures for stabilization by means of convection drying. The invention also relates to the amorphous, microscopically homogeneous products which are obtained by this process, are in the form of powders and have a uniform geometric, in particular spherical, shape. The invention furthermore relates to the use of substance mixtures for stabilizing biologically active material, in particular proteins by means of spray drying.

The invention relates to a rapid and readily reproducible process for producing dry, amorphous products which, besides biologically active, in particular therapeutically active, material, contain substance mixtures for stabilization by means of convection drying. The invention also relates to the amorphous, microscopically homogeneous products which are obtained by this process, are in the form of powders and have a uniform geometric, in particular spherical, shape. The invention furthermore relates to the use of substance mixtures for stabilizing biologically active material, in particular proteins by means of spray drying.

It is well known that proteins, especially human proteins, can be stabilized in solid preparations by a large number of substances, preferably by sugars or combinations of sugars and amino acids.

Various processes and formulations for producing dry, biologically or therapeutically active materials are described. By dry materials are meant substances and substance mixtures which have a residual moisture content not exceeding 8% (g/g), preferably not exceeding 4% (g/g), particularly preferably not exceeding 2%. Freeze-drying processes are widely used for producing such formulations [F. Franks, Cryo Lett. 11, 93-110, (1990); M. J. Pikal, Biopharm. 3 (9), 26-30 (1990); M. Ilora, Pharm. Research 8 (3), 285-291 (1992); F. Franks, Jap. J. Freezing Drying 38, 15-16, (1992)] but have the specific disadvantages of freeze-drying. They consume large amounts of energy, require the use of refrigerants, some of which are environmentally harmful (frigens), and are time-consuming because it is often necessary to remove relatively large volumes of ice by sublimation. The freezing step necessary for freeze-drying

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may be destabilizing for a large number of substances, especially for proteins. This process is therefore not applicable at all to some biological materials.

Alternatives to freeze drying for producing dry protein preparations are processes which dry the material by using heat and/or vacuum [F. Franks, R. M. H. Hatley: Stability and Stabilization of Enzymes; Eds. W. J. J. von den Teel, A. Harder, R. M. Butlaar, Elsevier Sci. Publ. 1993, pp. 45 - 54; B. Roser, Biopharm, 4 (9), 47-53 (1991); J. F. Carpenter, J. H. Crowe, Cryobiol. 25, 459 - 470 (1988)]. Examples which may be mentioned in this connection are vacuum drying with or without use of elevated temperature, spray-drying processes in a wide variety of modifications, including combined use of vacuum and spraying techniques, and drum drying and other thin-film drying processes.

J. F. Carpenter, J. H. Crowe, Biochemistry 28, 3916-3922 (1989); K. Tanaka, T. Taluda, K. Miyajima, Chem. Pharm. Bull. 39 (5), 10-94 (1991), DE 35 20 228, EP 0 229 810, WO 91/18091, EP 0 383 569 and US 5,290,765 describe preparations which contain sugars or sugar-like substances. However, the production of dry, carbohydrate-containing preparations by means of freeze or vacuum drying, especially of sugar preparations, is associated with disadvantages in the state of the art. These include, inter alia, high energy consumption for drying to an acceptable residual moisture content, extended process times at low drying temperatures, formation of highly viscous, water-containing masses (called „rubber") or glassy melts whose glass transition temperatures are below room temperature. The disadvantages described above significantly influence the stability of biological materials in such preparations.

It is also evident from the literature cited above that preparations suitable for stabilizing proteins should have glassy, that is to say amorphous, structures whose glass transition temperature is above the intended storage

temperature. The glass transition temperature (Tg) is the temperature at which an amorphous or partially crystalline solid is converted from the glassy state into the fluid or viscous state and vice versa. This involves drastic changes in the viscosity and, associated therewith, in the diffusion coefficient and the kinetic mobility of the biological materials. Physical characteristics such as hardness and modulus of elasticity are changed, as are the thermodynamic functions of volume, enthalpy and entropy. The glass transition temperature of, for example, a sugar-containing composition and its residual water content are physically linked together in such a way that increasing residual amounts of water lead to declining glass transition temperatures and vice versa. It is thus possible to infer from measurement of the glass transition temperature, for example by differential scanning calorimetry (DSC), whether a preparation has a residual water content suitable for stabilization or, as stated above, a drying process is successful or not. Besides determining the glass transition temperature by means of DSC, the presence of amorphous structures can also be proved by means of X-ray diffraction investigations, optical and electron microscopic examinations.

It was therefore desirable to provide fully amorphous ancillary substance structures for biological or pharmaceutically active materials so that the embedded biological materials can also be kept stable at room temperature and over a long period. The ancillary substance structures should have a low residual moisture content which can be adjusted intentionally, and have a glass transition temperature which is as high as possible.

WO 97/15288 describes a process for stabilizing biological materials by means of drying processes without freezing, with which partially amorphous ancillary substance structures are obtained. The drying was carried out as vacuum drying (at slightly elevated temperatures < 50°C), although inhomogeneous products are obtained.

WO 96/32096 describes the production of a homogeneous, dispersible powder, which contains a human protein, carbohydrates and/or amino acids and other ancillary substances, for inhalation by means of spray drying. However, it has emerged that amorphous products are not obtained in any of the examples.

EP 0 682 944 A1 describes lyophilisates with pharmaceutically acceptable ancillary substances, consisting of a phase with the protein in amorphous mannitol and a second phase with crystalline alanine. However, these formulations cannot stabilize the biological materials sufficiently will over a lengthy period.

The invention was based on the object of developing a mild, flexible, readily reproducible, rapid and economic drying process for embedding biological materials, especially human proteins, and of finding stabilizing matrices suitable for this process. It is intended that it be possible with this process to produce fully amorphous and homogeneous products which allow stabilization of the biological materials over a long period.

One aspect of the present invention provides for a process for producing dry, amorphous products which, besides biologically active material, contain a substance mixture for stabilization, characterized in that a solution or suspension of biological material and the substance mixture consisting of one, two or all of the following components (a), (b) and (c): (a) a carbohydrate and at least one amino carboxylic acid or derivatives thereof, (b) at least two amino carboxylic acids or derivatives thereof, (c) at least one amino carboxylic acid or a plurality of amino carboxylic acids or derivatives thereof, is produced and dried by means of convection drying with adjustment of a relative moisture content of < 70% (g/g) in the stationary phase at an inlet air temperature of 50 - 300°C.

The object of the invention, of providing an efficient process for producing amorphous preparations which contain biological materials, is achieved by means of convection drying, in particular by means of spray drying, under the conditions stated herein and with the substance mixtures stated herein. The invention relates in particular to a process for producing dry, amorphous products which, besides biological material, in particular therapeutically active material, contain substance

mixtures for stabilization, which is characterized in that a solution or suspension of biological material and a substance mixture consisting of (a) a carbohydrate and at least one zwitterion with polar or apolar radical or derivatives thereof, and/or (b) at least two zwitterions with polar or apolar radicals or derivatives thereof, and/or (c) at least one zwitterion with

polar or apolar radical or a plurality of zwitterions with polar or apolar radicals or derivatives thereof, is produced and dried by means of convection drying with adjustment of a relative moisture content of < 70%, preferably < 40%, in particular < 20%, in the stationary phase at an inlet air temperature of 50 - 300°C, preferably < 200°C. This manner of drying proves to be particularly advantageous in relation to the stability of the biological materials in the formulations and ensures yields > 90%.

The zwitterions with polar or apolar radicals which are preferably employed are amino carboxylic acids. The substance mixtures employed of group (a) comprise, preferably, mono-, oligo-, polysaccharides, arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine and/or derivatives thereof. The substance mixtures of group (b) comprise, preferably, arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine and/or derivatives thereof. The zwitterions of group (c) are preferably employed in the form of their salts. Preferably used are the salts of arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine and/or derivatives thereof.

Biologically active materials for the purpose of the invention are one or more substances of the groups of proteins, peptides, glycoproteins, lipoproteins, enzymes, coenzymes, antibodies, antibody fragments, virus constituents, cells and cell constituents, vaccines, DNA, RNA, biological therapeutic and diagnostic agents or derivatives thereof.

It is possible where appropriate to add to the solution or suspension of biological material and the substance mixture of groups (a) and/or (b) and/or (c) conventional ancillary substances from the groups of buffers, surfactants, antioxidants, isotonicizing agents, preservatives.

It is possible by spray drying with the features stated herein to modify carbohydrates, amino acids or derivatives thereof which can be dried with difficulty in such a way that they can be dried, or to mix carbohydrates, amino acids or derivatives thereof with a substance or a substance mixture which increase the Tg so that drying becomes possible and the resulting ancillary substance structure is amorphous and is outstandingly suitable for embedding biological materials. Vacuum drying of comparable formulas results in lower glass transition temperatures.

It has been found that in the case of carbohydrates, especially sugars such as, for example, sucrose, fructose, which indeed form amorphous structures after spraying from aqueous or organic solution into a hot air bed, but have low glass transition temperatures (< 20°C) and therefore result in yields which are extremely economically unfavourable on drying, and have low stability on storage, the latter in particular in relation to the retention of amorphous structures, the Tg is increased so much (≥ 20°C) by addition of zwitterions or derivatives thereof that they can be dried in good yield, and the amorphous structure of the carbohydrates or of the complete formulation is retained or stabilized.

It has furthermore emerged, surprisingly, that it is possible by adding zwitterions or derivatives thereof to obtain carbohydrates such as, for example, mannitol, after the spraying from aqueous or organic solution into a hot air bed, in an amorphous structure as is necessary for stabilizing biological materials. At the same time, good yields are achieved therein. This result is surprising since

no amorphous structures are obtained when the process is carried out without addition of zwitterions.

On the other hand, it has been found that even zwitterions or derivatives thereof which, although they can be dried after spraying from aqueous or organic solution into a hot air bed, are not obtained in amorphous form from this, are obtained in a fully amorphous form on addition of carbohydrates or derivatives thereof.

Amorphous structures are also obtained when zwitterions or derivatives thereof which, although they can be dried after spraying from aqueous or organic solution into a hot air bed, are not obtained in a fully amorphous form from this, can be converted by suitable admixtures of one or more zwitterions into a fully amorphous form. To produce the amorphous structure it is unnecessary to choose only combinations of zwitterions with polar radicals and apolar radicals; on the contrary it is also possible to employ combinations of zwitterions with only polar or only apolar radicals.

It has further emerged that one or more zwitterions with polar or apolar radicals or derivatives thereof which, although they can be spray-dried, are not obtained in amorphous form, can be converted by specific adjustment of the pH of the solution or suspension before the convection drying into the amorphous state, preferably by adjusting to a pH of 7.0 - 7.5. A specific adjustment of the pH of the solution before the spray drying can also be worthwhile in those cases (variants a and b) where, although amorphous structures are obtained, the stability of the protein in the amorphous structure is to be further improved or the amorphous structure of the sprayed products is to be further increased. Such an adjustment of the pH may also be necessary for physiological reasons.

The skilled person is able, by suitable combination of the variants mentioned, to increase significantly further

the effects already achieved. The teaching of the patent allows him to select a zwitterion with polar or apolar radical so that the dried substance mixture has a raised glass transition temperature and/or an amorphous structure by comparison with a substance mixture without a corresponding addition.

The products obtained with the process according to the invention are amorphous and microscopically homogeneous powders in a particle size range from 0.0005 mm to 1 mm, preferably from 0.001 mm to 0.1 mm. The process according to the invention allows preferably spherical particles to be obtained in a particle size range which is adjustable and can be reproduced surprisingly well. The resulting products have a glass transition temperature $\geq$ 20°C, preferably $\geq$ 40°C, and a residual moisture content < 8% (g/g), preferably < 4% (g/g). The amorphous structure is furthermore retained over storage times of at least 12 months. Compared with lyophilisates, the products have an apparent density which is higher by at least a factor of 1.15 (15%) than lyophilisates and, compared with products from freeze or vacuum drying, have significantly lower crystalline contents for the same formulation.

The amorphous products, which preferably contain proteins as biological materials, are produced according to the invention by convection drying, in particular by spray drying or spray granulation, by producing a solution or suspension of the biological material and the substance mixture, and carrying out the convection drying at an inlet air temperature of 50 - 300°C, preferably < 200°C, it having emerged that the relative moisture content in the stationary phase must be adjusted to < 70%, preferably < 40%, in order to obtain a defined product moisture content of < 4%. The process according to the invention thus permits the required residual moisture content in the final products to be adjusted intentionally.

It is possible according to the invention for the convection drying to take place by means of fluidized drying, lift air drying or flight drying. Spray or fluidized bed drying is particularly preferably used according to the invention.

In the spray drying, the material to be dried is sprayed in a manner known per se as solution or suspension through nozzles or by means of a rapidly rotating atomizer disc to give a mist of droplets at the upper end of a wide cylindrical container. The resulting mist of droplets is mixed with hot air or an inert gas, which are passed around the atomizing zone into the dryer. If a solution is atomized under otherwise identical conditions by means of a two-component nozzle or disc, although the particle size distribution of the spray embedding is narrower with disc atomization than with nozzle atomization, it is shifted into the coarser region.

Suitable atomizing devices are swirl pressure nozzles, pneumatic nozzles (two-component/three-component nozzles) or centrifugal atomizers. Although pneumatic nozzles require the greatest energy consumption for atomization per kg of liquid, these nozzles are particularly suitable because of their flexibility, for example for achieving particular particle size ranges or particular particle shapes. The process can also be carried out by means of the use of a three-component nozzle technique. It is possible thereby to atomize two liquids simultaneously.

This makes two variants of the atomization possible:

Variant 1

The two liquids are fed separately and, shortly before the atomization, mixed and then atomized. This variant is preferably used when the mixtures of two components are stable for only a short time in one liquid phase.

Variant 2

The two liquids are fed separately, atomized separately and mixed before entering the nozzle orifice. This variant can be used for two immiscible solutions or where the stability of the components is ensured only in the solid state.

It was possible to use these specific types of atomization for the invention just as well as classical two-component atomization.

A process according to the invention is optimal with an inlet air temperature in the range between 100°C and 180°C. Since there is also a risk of decomposition of the spray embedding as the inlet air temperature increases, higher temperatures $\geq$ 200°C are normally not productive but can certainly be considered for specific applications. It is surprising that the stability of the biological materials in the formulations is very good although the hot air used according to the invention for the drying preferably has a temperature of > 100°C.

The spraying of the solution after the drying results in preferentially spherical particles in an adjustable and reproducible particle size range. Spherical shapes with favourable flow properties and a particular particle size range are precisely those particularly advantageous for many types of pharmaceutical application.

The drying times with the process according to the invention are not more than one minute.

It is also possible according to the invention to produce granules by spraying the solution of biological material and substance mixture onto a carrier with a particle size range from 0.010 mm to 10 mm, preferably 0.1 to 1 mm.

It is thus possible with the process according to the invention, by using the stated substance mixtures, to improve

crucially the drying of carbohydrate-containing compositions. The formulations according to the invention contain as main component a carbohydrate, preferably sugar, and one or more zwitterions with polar or apolar radicals or derivatives thereof, with the glass transition temperature of the sugar being distinctly increased by this zwitterion addition.

Formulations in which the main component are zwitterions with polar or apolar radicals or derivatives thereof can be converted into stable amorphous forms by addition of carbohydrates.

It is also possible as an alternative to the carbohydrates to use zwitterions with polar or apolar radicals or derivatives thereof or mixtures thereof. These formulations can be composed of at least 2 zwitterions or derivatives thereof with polar radicals, at least 2 zwitterions or derivatives thereof with apolar radicals or of at least one zwitterion with polar and apolar radical.

Amorphous and dry formulations can also be obtained by specific adjustment of the pH of the solution of zwitterions with polar or apolar radicals or derivatives thereof, alone or in combination.

Substance mixtures which can be preferably employed according to the invention consist of at least two substances selected from sucrose, L-arginine, L-phenylalanine, L-aspartic acid, L-isoleucine and derivatives thereof.

Besides the compositions indicated in the examples, the following substance mixtures have also proved particularly suitable as matrix for the formation of sprayed products according to the invention:

Mixture (formula) 1:
Sucrose, L-arginine and L-phenylalanine,

Mixture (formula) 2:
L-Arginine, L-aspartic acid and L-isoleucine,

Mixture (formula) 3:
L-Arginine and L-phenylalanine,
Mixture (formula) 4:
L-Arginine, L-phenylalanine and L-aspartic acid.

The invention also relates to the use of the amorphous products produced according to the invention for producing diagnostic or therapeutic compositions by further processing them where appropriate with conventional ancillary substances and excipients.

Example 1

The carbohydrate and the amino acid (AA) were dissolved in water at RT. Adjustment of the pH may be necessary depending on the biological material used. This solution is then spray dried.

It is evident from the following table that, for example, sucrose or fructose cannot be dried in economically good yields because of the low glass transition temperature (1.1 and 1.5), whereas the solutions with AA addition result after the drying as fine-particle dry powders in good yields (1.2 - 1.4 and 1.6). It is further evident from the table that carbohydrates such as, for example, mannitol, which after the drying normally do not form amorphous structures and result in economically favourable yields (1.7), on addition of zwitterions or derivatives thereof form an amorphous structure and result in good yields as are necessary for the stabilization of biological materials (1.8).

Carbohydrates with addition of zwitterions with polar/apolar radicals

Example	Carbohydrate mg/ml	Amino acid mg/ml	Residual water content %	Glass transition temperature °C Crystal structure State of aggregation
	Sucrose	L-Arginine		
(1.1)	275	0	2.8	<20°C X-ray amorphous tacky mass
	Sucrose	L-Arginine		
(1.2)*	100	5	2.4	≥20°C X-ray amorphous Powder
	Sucrose	L-Phenyl-alanine		
(1.3)	100	5	2.8	≥20°C X-ray amorphous Powder
(1.4)	100	20	2.5	≥20°C X-ray amorphous Powder
	Fructose	L-Phenyl-alanine		
(1.5)	275	0	2.3	<20°C X-ray amorphous tacky mass
(1.6)	100	5	4.0	≥20°C X-ray amorphous Powder
	Mannitol	L-Arginine/ L-phenyl-alanine		
(1.7)	55	0	0.4	- crystalline powder
(1.8)*	100	10/ 10	2.5	≥20°C X-ray amorphous Powder

* pH adjusted to 7.3 ± 0.2

Example 2

The amino acid and the carbohydrate were dissolved in water at RT and spray dried. It is evident from the following table that the pure AA results in a crystalline crystal

structure (2.1 and 2.4), but amorphous structures are obtained on addition of carbohydrate (2.2, 2.3, 2.5).

Zwitterions with polar/apolar radicals on addition of carboyhydrates

Example	Amino acid mg/ml	Carbo-hydrate mg/ml	Residual water content %	Glass transition temperature °C Crystal structure State of aggregation
	L-Arginine	Methyl-hydroxy-propyl-cellulose 2910		
(2.1)	55	0	10.2	- crystalline powder
(2.2)	20	4	7.2	≥20°C X-ray amorphous powder
	L-Arginine	Sucrose		
(2.3)	20	4	6.4	≥20°C X-ray amorphous powder
	L-Phenyl-alanine	Sucrose		
(2.4)	55	0	0.4	- crystalline powder
(2.5)	20	4	4.6	≥20°C X-ray amorphous powder

Example 3

The amino acids were dissolved in water at RT and spray dried. It is evident from the table that the pure AA results in a crystalline structure (3.1-3.4), but amorphous structures are obtained on addition of a second AA (3.5-3.8). In Examples 3.9-3.11, the Tg values of vacuum dryings are indicated. The Tg values on vacuum drying of comparable formulas are distinctly below the values in the process according to the invention.

Zwitterions with polar/apolar radicals on further addition of zwitterions with polar/apolar radicals

Example	Amino acid mg/ml	Amino acid mg/ml	Residual water content %	Glass transition temperature °C Crystal structure State of aggregation
	L-Arginine			
(3.1)	55	0	10.2	- crystalline powder
	L-Isoleucine			
(3.2)	21.7	0	0.4	- crystalline powder
	L-Phenyl-alanine			
(3.3)	55	0	0.4	- crystalline powder
	L-Aspartic acid			
(3.4)	6.7	0	0.3	- crystalline powder
	L-Phenyl-alanine	L-Isoleucine		
(3.5)	20	4	1.2	≥20°C X-ray amorphous powder
	L-Arginine	L-Phenyl-		

		alanine		
(3.6)	20	4	5.7	≥20°C X-ray amorphous powder
	L-Arginine	L-Aspartic acid		
(3.7)	4	20	5.5	≥20°C X-ray amorphous powder
	L-Arginine	L-Aspartic acid/L-Isoleucine		
(3.8)	40	22 10	4.2	≥20°C X-ray amorphous powder

Vacuum drying

Example	Amino acid mg/nl	Amino acid mg/ml	Residual water content %	Glass transition temperature °C
	L-Arginine	L-Phenyl-alanine		
3.9	33.4	7.9	9.9	1.3
3.10	34.8	6.6	10.7	0.0
3.11	35.8	5.6	10.0	1.3

Example 4

The amino acid was dissolved in water at RT and spray dried. It is evident from the following table that an X-ray-amorphous structure is formed by specific adjustment of the pH (4.1 and 4.3), otherwise only a crystalline structure is obtained (4.2 and 4.4).

Zwitterions with polar/apolar radicals

Example	Amino acid mg/ml	Amino acid mg/ml	Residual water content %	Glass transition temperature °C Crystal structure State of aggregation
	L-Arginine			
(4.1)	55 pH 7.2 adjusted with H_3PO_4	0	5.1	≥20°C X-ray amorphous Powder
	L-Arginine			
(4.2)	55	0	10.2	- crystalline powder
	L-Aspartic acid			
(4.3)	8.3 pH 7.2 adjusted with NaOH	0	0.5	≥20°C X-ray amorphous Powder
	L-Aspartic acid			
(4.4)	6.7	0	0.3	- crystalline powder

Example 5

The carbohydrate, the AA and other ancillary substances were dissolved in water at RT, adjusted to pH 7.3 ± 0.2 and spray dried.

The following table shows optimized active drug formulas according to the process according to the invention (5.2-5.6). A placebo formula (5.1) was used for comparison. No decomposition products were shown by any of the formulas after the drying, it being possible to detect high molecular weight (HMW) aggregates and EPO dimers not exceeding 0.2% in formulas 5.2-5.6. This value is not exceeded even after storage for 3 months (shown by Example 5.3).

By contrast, a formula not according to the invention shows a very high content of high molecular weight (HMW) aggregates and EPO dimers even immediately after the drying (5.7).

Example	EPO U/ Carbohydrate mg/ml	Amino acids/ ancillary substance mg/ml	Residual water content %	Glass transition temperature °C Crystal structure State of aggregation
	- Sucrose	L-Arginine/ L-Phenyl-alanine/ Tween 20		
(5.1)	- 100	20/ 20/ 0.2	2.8	≥ 20°C X-ray amorphous powder
	EPO/sucrose	L-Arginine/ L-phenyl-alanine/ Tween 20		
(5.2)	7000/ 50	10/ 10/ -	3.5	≥ 20°C X-ray amorphous powder
(5.3)	7010/ 50	10/ 10/ 0.1	2.4	≥ 20°C X-ray amorphous powder
	EPO/ Sucrose	L-Arginine/ L-phenyl-alanine/ Tween 20		
(5.4)	14020/ 100	20/ 20/ 0.2	2.9	≥ 20°C X-ray amorphous powder
	EPO/ -	L-Arginine/ L-aspartic acid/ L-iso-leucine/ Tween 20		
(5.5)	5010/ -	30/ 10/ 10/ 0.1	4.3	≥ 20°C X-ray amorphous powder
	EPO/ -	L-Arginine/ L-aspartic acid/ L-phenyl-alanine/ Tween 20		
(5.6)	5010/ -	30/ 10/ 10/ 0.1	4.4	≥ 20°C X-ray amorphous powder

Storage stability of Example 5.3 in refrigerator, at RT and 40°C for 3 months

	HMW aggregates			EPO dimers		
	Fridge (4-6°C)	RT (20-22°C)	40°C	Fridge (4-6°C)	RT (20-22°C)	40°C
5.3						
Initial		<0.1%			<0.1%	
After 2 months	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
After 3 months	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	0.1%

Content of HMW aggregates and EPO dimers in a formula not according to the invention immediately after drying:

Example	**EPO U/ carbo-hydrate mg/ml** EPO/ lactose	**Residual water content %**	**HMW aggregates %**	**EPO dimers %**
(5.7)	7010/ 50	3.4	9	2

Example 6

The following Examples 6 to 12 illustrate the effect of the chosen conditions in the process according to the invention on the final products. The following formulas 1 to 4 were investigated:

Mixture (formula) 1:
Sucrose, L-arginine and L-phenylalanine (5:1:1)

Mixture (formula) 2:
L-Arginine, L-aspartic acid and L-isoleucine (3:1:1)

Mixture (formula) 3:
L-Arginine and L-phenylalanine (1:1)

Mixture (formula) 4:
L-Arginine, L-phenylalanine and L-aspartic acid (3:1:1)

Spray drying of substance mixtures 1 to 4:

Starting materials	Composition of the solution			
Mixture	1	2	3	4
Sucrose	50 mg/ml			
L-Arginine	10 mg/ml	30 mg/ml	20 mg/ml	30 mg/ml
L-Phenyl-alanine	10 mg/ml		20 mg/ml	10 mg/ml
L-Aspartic acid		10 mg/ml		10 mg/ml
L-Isoleucine		10 mg/ml		

Example 7

Spray drying with different inlet air temperatures

The four mixtures were spray dried at three different inlet air temperatures, namely at 100°C, 140°C and 180°C. A very important parameter in the spray drying is the rel. moisture content in the stationary phase of the spray drying. The stationary phase is regarded as being the drying section where the process of drying the sprayed particles is complete and the maximum temperature stress on the dried sprayed particles is reached. The relative moisture content in the stationary phase determines the moisture content of the product after the drying. The relative moisture content to be chosen in this case depends on the composition of the formulation. The relative moisture content in the stationary phase for the four mixtures was chosen according to the invention to be very low at less than 40% (specifically about 10% in this case). This established whether spray drying of

mixtures 1 - 4 is still in fact possible. Spray drying of the four mixtures was possible satisfactorily under the abovementioned conditions. In all cases, fine-powder spray embeddings (SE) were obtained in good yield (> 90%). There were no deposits on the tower cone and the pipelines, and discharge of the products was possible satisfactorily despite the low dust/air ratios (<< 50 g/Nm^3 (STP)).

Relative moisture content 10%

Inlet air temperature	Rel. moisture content, stationary phase	Water vaporization rate	Solid (from 7% strength solution)
°C	%	Approx. g/h	approx. g/h
60	10	100	7.5
100	10	600	45.2
140	10	1000	75.3
180	10	1400	105.4

Example 8

Tests on the spray embedding products (SE)

a) pH, density, water content, osmolality

Mixture	Inlet air temperature	SE water content	PH Initial solution / SE	Density Initial solution/ SE	Osmolality Initial solution/ SE
	°C	%		g/cm^3	mOsm/kg
Mixture 1	100	3.2	7.4/7.44	1.025/ 1.023	270/272
Mixture 1	140	3.0	7.4/7.44	1.025/ 1.022	270/270
Mixture 1	180	3.0	7.4/7.43	1.025/ 1.020	270/273
Mixture 2	100	3.9	7.4/7.44	1.017/ 1.021	292/270
Mixture 2	180	2.6	7.4/7.44	1.017/ 1.022	292/279
Mixture 3	100	2.4	7.4/7.43	1.013/ 1.010	216/213

Mixture 3	180	2.7	7.4/7.43	1.013/ 1.011	216/212
Mixture 4	100	3.6	7.4/7.38	1.018/ 1.023	274/254
Mixture 4	180	2.7	7.4/7.37	1.018/ 1.023	274/254

The spray embeddings dissolved in water gave identical values for the pH, the density and the osmolality as for the initial solution. The water content of the spray embeddings decreased slightly as the inlet air temperature increased, although the rel. moisture content in the stationary phase was kept constant. In particular, mixture 1 showed an almost constant water content at all inlet air temperatures.

b) Crystal structure

Irrespective of the inlet air temperatures, all the spray embeddings are X-ray amorphous by comparison with the initial mixtures.

c) Electron micrographs

The electron micrographs of the spray embeddings from mixture 1 show that the SE particles are in the form of almost ideal complete spheres, with the surface changing from a texture resembling a golf ball to a smooth appearance with increasing inlet air temperature. To demonstrate that complete spheres are present, the spray embeddings were ground. The completely spherical shape can be deduced unambiguously from the fragments. The mode of atomization, nozzle or disc atomization, has no effect whatsoever on the shape of the SE particles.

d) Particle size distribution

Mixture 1 was used to demonstrate that the particle size distribution remains approximately constant at different spraying rates.

Inlet air temperature	Rel. moisture content, stationary phase	Spraying rate	Particle size d10/d50/d90	Particle size RRSB-d'
°C	%	g/h	µm	µm
100	10	640.0	0.8/3.7/9.7	5.7
140	10	1035.0	0.6/5.3/12.6	6.6
180	10	1455.0	0.7/4.0/11.9	6.3

It was also established that virtually identical particle size distributions are obtained with the same inlet air temperature and approximately the same spraying rate.

Inlet air temperature	Rel. moisture content, stationary phase	Spraying rate	Particle size d10/d50/d90	Particle size RRSB-d'
°C	%	G/h	µm	µm
100	10	566.0	0.7/4.0/10.5	5.8
100	10	640.0	0.8/3.7/9.7	5.7
140	10	1067.5	0.8/4.0/11.6	6.2
140	10	1035.0	0.6/5.3/12.6	6.6

Example 9

Measurement of the glass transition temperature (Tg) by differential scanning calorimetry (DSC)

To determine the glass transitions of the dried samples, and the crystallization and melting peaks, a DSC 7 apparatus from Perkin-Elmer* (Überlingen) with CCA 7 low-temperature control with liquid nitrogen (Messer, Griesheim) and a TAC 7/DX signal transducer was used. The weights of the samples were between 5 and 20 mg, weighed into aluminium crucibles (Perkin-Elmer) previously weighed using an autobalance AD4 microbalance (Perkin-Elmer). The crucibles

* Trademark

were then tightly closed with a lid (Cover, Perkin-Elmer) using a universal closure press (Perkin-Elmer), placed in the measurement cell flushed with nitrogen and measured at a heating rate of 10°C/min.

The Tg of mixture 1 were determined by means of DSC. With a water content < 4%, the respective Tg were advantageously far above room temperature, which means that the mixtures are very suitable for stabilizing biological material, in particular human proteins.

Inlet air temperature	SE water content	Tg
°C	%	°C
100	3.2	57.6
140	3.0	58.8
100	3.8	57.0
140	7.5	28.2

Example 10

Differing rel. moisture content in the stationary state

It is shown with mixture 1 how far the rel. moisture content of the stationary phase influences, with conditions which are otherwise constant, the product moisture content and thus the Tg.

Inlet air temperature	Rel. moisture content, stationary phase	Water content	Tg
°C	%	%	°C
140	4	1.5	67.7
140	10	3.0	58.8
140	25	5.9	31.7
140	33	6.5	29.1
140	36	7.5	28.2

Example 11

Effect of the initial concentration of the solution on the spray embedding

An increase in the initial concentration of the solution is possible in principle up to the solubility limits determined by the ancillary substances and results in almost the same physical properties of the spray embeddings as from a 7% strength solution. This is illustrated by the following table based on mixture 1.

Inlet air temperature	Concen-tration of the solution	Tg/water content pH	Particle size d10/d50/d90	Particle size RRSB-d'
°C	%	°C/%	µm	µm
100	15	57.3/3.6/7.5	0.8/4.6/12.9	6.7
100	15	52.8/3.4/7.44	0.7/4.6/10.8	6.0
100	7	57.6/3.2/7.38	0.8/3.7/9.7	5.7

Example 12

a) Testing of various atomization units (two-component nozzle, atomizer disc) using mixture 1

The use of different atomization units has effects on the particle size distributions of the spray embeddings.

Inlet air temperature	Atomization unit	Atomization pressure or speed of rotation	Particle size d10/d50/d90	Particle size RRSB-d'	Gradient of the line in the RRSB grid
°C	µm	Bar/rpm	µm	µm	1
100	two-comp. nozzle	3 bar	0.8/3.7/9.7	5.7	1.018
140	two-comp. nozzle	3 bar	0.6/5.3/12.6	6.6	1.052
180	two-comp. nozzle	3 bar	0.7/4.0/11.9	6.3	0.994
100	disc	max.	1.7/11.9/23.3	15.3	1.238

Disc atomization is unsuitable for pulmonary uses of the SE products, which require particle sizes < 10 µm. In addition, the flexibility of the two-component nozzle is considerably greater than that of a disc for shifting particle size ranges. A disadvantage is that on sterile operation with two-component atomization it is necessary for the atomization medium to be sterilized by filtration. The other physical parameters of the SE products do not depend on the mode of atomization, appearance included. Atomization media which can be employed are the known media such as compressed air or inert gases such as, for example, noble gases (neon, argon etc.) or carbon dioxide.

b) Different nozzle combinations

The specific nozzle combinations (three-component nozzles) are used for feeding and atomizing two liquids simultaneously.

The spray embeddings obtained with both variants of the three-component nozzle had physical parameters agreeing with those of the spray embeddings obtained from the two-component atomization. Even the Tg and the X-ray-amorphous form were identical.

Example 13

Reproducibility with identical/different batch sizes

The process is reproducible with identical or different batch sizes as shown by the example of mixture 1. The SE products obtained in all cases have physical parameters of the spray embeddings which are within very narrow limits. It is thus possible to apply the results of the trial batches directly to larger batches, and hence a process ready for production is available.

Inlet air temperature °C	Batch size Items	Crystal structure	Particle size d10/d50/d90 µm	Particle size RRSB-d' µm	DSC Tg/ water content °C/%
100	1000	X-ray amorphous	0.8/3.7/ 9.7	5.7	57.6/3.2
140	1000	X-ray amorphous	0.6/5.3/ 12.6	6.6	58.8/3.0
180	1000	X-ray amorphous	0.7/4.0/ 11.9	6.3	57.0/3.0
140	2000	X-ray amorphous	0.8/4.0/ 11.6	6.2	58.8/2.8
100	300	X-ray amorphous	/.7/4.0/ 10.5	5.8	57.0/3.2

WE CLAIM:

1. A process for producing dry, amorphous products which, besides biologically active material, contain a substance mixture for stabilization, characterized in that a solution or suspension of biological material and the substance mixture consisting of one, two or all of the following components (a), (b) and (c):

(a) a carbohydrate and at least one amino carboxylic acid or derivatives thereof,

(b) at least two amino carboxylic acids or derivatives thereof,

(c) at least one amino carboxylic acid or a plurality of amino carboxylic acids or derivatives thereof,

is produced and dried by means of convection drying with adjustment of a relative moisture content of < 70% (g/g) in the stationary phase at an inlet air temperature of 50 - 300°C.

2. The process according to Claim 1, characterized in that the solution or suspension prepared according to variant (c) is adjusted to a specific pH before the convection drying.

3. The process according to any one of Claims 1 to 2, characterized in that the substance mixture is employed of group (a) which comprises mono-, oligo-, polysaccharides, arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine or derivatives thereof.

4. The process according to any one of Claims 1 to 2, characterized in that the substance mixture is employed of group (b) which comprises arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine or derivatives thereof.

5. The process according to any one of Claims 1 to 2, characterized in that the substance mixture is employed of group (c).

6. The process according to Claim 5, characterized in that the substance mixture is employed of group (c) which comprises the salts of arginine, aspartic acid, citrulline, glutamic acid, histidine, lysine, acetylphenylalanine ethyl ester, alanine, cysteine, glycine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine or derivatives thereof.

7. The process according to any one of Claims 1 to 6, characterized in that one or more substances of the groups of proteins, peptides, glycoproteins, lipoproteins, enzymes, coenzymes, antibodies, antibody fragments, virus constituents, cells and cell constituents, vaccines, DNA, RNA, biological therapeutic and diagnostic agents or derivatives thereof are employed as biological material.

8. The process according to any one of Claims 1 to 7, characterized in that conventional ancillary substances from the groups of buffers, surfactants, antioxidants, isotonicizing agents and preservatives are added to the solution.

9. The process according to any one of Claims 1 to 8, characterized in that the drying takes place by fluidized drying, lift air or flight drying.

10. The process according to any one of Claims 1 to 8, characterized in that the drying takes place by spray or fluidized bed drying.

11. The process according to any one of Claims 1 to 10, wherein the biologically active material comprises therapeutically active material.

12. The process according to any one of Claims 2 to 11, wherein the specific pH is a pH of 7.0 - 7.5.

13. Amorphous, microscopically homogeneous products containing a biologically active material and a substance mixture for stabilization, with a glass transition temperature $\geq 20°C$ and a residual moisture content $< 8\%$ (g/g) obtained by the process a defined in any one of Claims 1 to 12.

14. The amorphous products according to Claim 13, characterized in that they have a glass transition temperature $\geq 40°C$ and a residual moisture content $< 4\%$ (g/g).

15. The amorphous products according to Claim 13 or 14, characterized in that they are in the form of powders in a particle size range of from 0.0005 mm to 1 mm.

16. The amorphous products according to Claim 15, wherein the particle size range is from 0.001 to 0.1 mm.

17. A use of amorphous products of Claims 13 to 16 for producing diagnostic or therapeutic compositions.

18. A use of substance mixtures consisting of one, two or all of the following components (a), (b) and (c):

(a) a carbohydrate and at least one amino carboxylic acid or derivatives thereof,

(b) at least two amino carboxylic acids or derivatives thereof,

(c) at least one amino carboxylic acid or a plurality of amino carboxylic acids or derivatives thereof,

for stabilizing biologically active material by means of spray drying with adjustment to a relative moisture content of $< 70\%$ in the stationary phase at an inlet air temperature of 50 - 300°C.

19. The use of Claim 18, wherein the biologically active material is therapeutically active material.

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(57) Abrégé/Abstract:
Processes for spray-drying water-soluble and water-swellable vinyl-addition polymer-containing dispersions, emulsions and microemulsions to obtain substantially dry water-soluble or water-swellable polymer particles, compositions of substantially dry water-soluble or water-swellable polymer particles, methods of agglomerating spray-dried polymer particles, and methods of using spray-dried polymer particles and agglomerates in water-treating, mining, paper, food processing, soil conditioning, solution thickening, biotechnological, and oil recovery applications are disclosed.

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(54) Title: SPRAY-DRIED POLYMER COMPOSITIONS AND METHODS

(57) Abstract

Processes for spray-drying water-soluble and water-swellable vinyl-addition polymer-containing dispersions, emulsions and microemulsions to obtain substantially dry water-soluble or water-swellable polymer particles, compositions of substantially dry water-soluble or water-swellable polymer particles, methods of agglomerating spray-dried polymer particles, and methods of using spray-dried polymer particles and agglomerates in water-treating, mining, paper, food processing, soil conditioning, solution thickening, biotechnological, and oil recovery applications are disclosed.

SPRAY-DRIED POLYMER COMPOSITIONS AND METHODS

Field of the Invention

This invention relates generally to processes for spray drying dispersions, emulsions and microemulsions containing water-soluble or water-swellable polymers to obtain substantially dry water-soluble or water-swellable polymer particles, compositions of substantially dry water-soluble or water-swellable polymer particles, and methods of using said polymer particles in water-treating, mining, paper, biotechnological, food processing, soil conditioning, solution thickening, and oil recovery applications.

Background of the Invention

High molecular weight, water-soluble and water-swellable polymers produced from such monomers as acrylamide are commercially important materials. These polymers find use as flocculants for mining operations to recover ore from slurries, water treating to remove suspended impurities etc., in agriculture as soil conditioners, and also in paper making to aid paper formation and in oil recovery industries.

Water-soluble and water-swellable polymers are generally commercially available in solution, dry, dispersion, water-in-oil emulsion, and water-in-oil microemulsion forms. In many cases polymer solutions are convenient, but may be limited to low molecular weight polymers and/or low solids levels because of the problem of handling viscous solutions of high solids, high molecular weight polymers. At very high solids and/or molecular weights, the solutions form gels that can be comminuted to form fine polymer gel particles that may be dissolved into water by the end-user. Although these comminuted gels typically contain up to about 20% water, they are frequently called "dry" polymers to distinguish them from the other product forms. In many cases the dry polymers exhibit long dissolution times and poor handling characteristics e.g. dusting. Although some handling problems may be mitigated by agglomeration see e.g. EP 0 277 018 A2; U.S. Patent Nos. 3,279,924; 3,275,449, 4,696,762; 5,171,781; both solutions and gels of water-soluble and water-swellable polymers may also suffer from the lack of a convenient method for post-reacting or functionalizing the polymer.

Another problem relates to blends of dry polymers, particularly when blending dry polymers having different particle sizes or particle size distributions. It is well known that dry polymer particles tend to stratify on handling and storage, with the larger particles

tending to settle towards the bottom of the container, and the smaller particles tending to be concentrated towards the top. Stratification may be inconvenient because differences in handling characteristics are encountered as a function of container depth. The stratification problem may be exacerbated when two different dry polymers are blended together, because the particle size distributions of the two products are generally not identical. Stratification on storage may affect blend product performance as the top of the container tends to become enriched in the polymer having the smaller particle size. For obvious reasons, changes in product performance as a function of storage depth are to be avoided, and it is generally preferred that each polymer be of similar particle size, see e.g. EP 479 616 A1 and U.S. Patent No. 5,213,693. However, when producing dry polymer by spray-drying, changes in production e.g. changes in dryer size, dryer temperature, bulk viscosity of the feed, atomizer type, etc. may affect particle size, and it may be difficult or impossible to achieve a desired particle size while simultaneously maintaining some other production parameter, so blends of spray-dried polymers may be adversely affected by stratification.

The advent of water-in-oil emulsion and water-in-oil microemulsion forms of water-soluble and water-swellable polymers solved some of these problems, e.g. blends of water-in-oil emulsions and water-in-oil microemulsions as disclosed in U.S. Patent Nos. 5,914,366; 5,763,530; and 5,763,523 do not tend to stratify, and high solids, high molecular weight, and relatively fast dissolution times may all be obtained simultaneously. In addition, unique functionalized polymers may be produced that cannot be practically manufactured by polymerization in solution. For instance, U.S. Patent Nos. 4,956,399; 4,956,400; 5,037,881; and 5,132,023, teach that functionalization of a water-soluble polymer contained in a water-in-oil microemulsion can be carried out to produce high molecular weight charged polymers with advantageous flocculation performance. The use of microemulsions, as opposed to emulsions, in polymer production provides improved polymer performance properties among other benefits. Hydrolyzed polyacrylamides with uniquely high molecular weight are disclosed in U.S. Patent No. 5,286,806. In U.S. Patent No. 4,767,540, very high molecular weight hydroxamate-functionalized polyacrylamide is disclosed, and novel charged organic polymer microbeads are disclosed in U.S. Patent Nos. 5,274,055 and 5,167,766. In addition, methods for esterifying (meth)acrylic acid polymer and, optionally, hydroxamating said polymers are disclosed in U.S. Patent No. 5,847,056.

Despite the many benefits provided by emulsion and microemulsion polymers,

transportation costs associated with such materials remain high and disposal of the oil and emulsifier in the emulsions may pose environmental concerns as secondary pollution. Moreover, many emulsion and microemulsion polymers tend to exhibit stability problems, e.g. detrimental changes in polymer properties and/or performance as a function of time. Although U.S. Patent Nos. 5,914,366; 5,763,530; 5,763,523; 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,274,055; and 5,167,766 mention non-solvent precipitation and stripping as methods of recovering dry polymer products from water-swellable or water-soluble polymer microemulsions or microemulsion-containing blends, these methods may produce a dry polymer with undesirable handling properties, poor dissolution times, low bulk density, etc. Practically, non-solvent precipitation and stripping may be inconvenient and expensive.

Water-soluble polymers may also be prepared in the form of suspensions or dispersions of polymer beads or droplets in a non-aqueous liquid e.g. oil. The reverse phase polymerization process described in U.S. 4,528,321 is said to form dispersions of water-soluble polymers. Water-soluble polymer dispersions, which may be azeotropically dried, are disclosed in U.S. Patent No. 4,628,078. U.S. Patent 4,506,062 discloses a reverse phase suspension polymerization process for the production of high molecular weight, water-soluble polymers and also reports that dry polymer beads may be obtained by azeotropic evaporation followed by filtration. However, a problem remains in that azeotropic distillation tends to be energy-intensive, and the filtering process may be hazardous or inconvenient.

Although dry polymers may be obtained from vinyl-addition polymer-containing water-in-oil emulsions, water-in-oil microemulsions or dispersions by such methods as precipitation in a non-solvent, stripping, etc., these methods may also be impractical for economic and environmental reasons because of difficulties in recovering, purifying and recycling the oil. Although the oil recovered from an emulsion or suspension polymerization may occasionally be recycled without further purification, as disclosed in U.S. 4,212,784 and JP 50-124979, in other cases e.g. S.I.R. H915 additional purification steps are necessary. The level of impurities in the oil is an important consideration, as certain polymerizations e.g. chain-growth polymerizations, or polymerizations used to make very high molecular weight polymers, are especially sensitive to even trace amounts of polymerization-debilitating substances. Particular problems are also encountered where the polymer has been formed from monomers in the presence of the oil or the oil has been heated or subjected to processing steps, which may have a tendency to deposit polymerization-debilitating impurities in the oil.

Spray-drying is the transformation of feed from a fluid state to a dried particulate form by spraying the feed into a hot drying medium, typically a hot gas. Spray-drying is widely used to produce a diverse range of products e.g. instant coffee, dried eggs, instant milk, household detergents, pharmaceutical products, pigments, cosmetics, starch, plastics, ceramics, etc. Typical spray-drying equipment, drying procedures, etc. are described in detail in known references e.g. "Spray Drying Handbook," by K. Master, 5th Ed., Longman Scientific, 1991.

Aqueous solutions of water-soluble polymers may be spray dried as in U.S. Patent Nos. 3,803,111 and 4,892,932. U.S. Patent Nos. 4,847,309 and 4,585,809 disclose processes for spray-drying acrylic polymer-containing emulsions, U.S. Patent No. 4,798,888 discloses a process for spray-drying a polysaccharide emulsion, U.S. Patent No. 4,816,558 discloses a process for spray-drying an aqueous dispersion of a synthetic resin and U.S. Patent No. 4,112,215 discloses a process for spray-drying an aqueous dispersion of a copolymer. U.S. Patent No. 5,025,004 discloses a process for spray-drying an emulsion of a water-insoluble polymer.

U.S. Patent No. 4,035,317 teaches that water-in-oil emulsions of water-soluble vinyl-addition polymers may be spray dried, under certain conditions, to produce free-flowing, non-dusting polymer particles which rapidly dissolve in water. Powders of polyacrylamide, acrylamide/acrylic acid copolymer, and acrylamide/dimethylaminopropyl methacrylate copolymers are described therein. The size range of the spray-dried products is such that none are smaller than about 325 mesh (about 40 microns), at least about 50% are larger than about 120 mesh (about 122 microns), and substantially none of the particles are larger than about 20 mesh (about 841 microns). These particles do not clump when added to water and dissolve much faster than traditional dry or gel particles of water-soluble polymers. When the spray-dried particles are either larger or smaller than this size range, however, they dissolve with difficulty. Although the invention of U.S. 4,035,317 was a significant advance in the art, a difficulty nevertheless remains with respect to certain polymers, in that the spray-drying methods of said patent gives polymers whose properties are undesirably changed relative to the emulsion or microemulsion form. Attempts to spray-dry Mannich polyacrylamides according to the teachings in the art resulted in polymer powder exhibiting reduced flocculation performance, compared to that of the corresponding polymers used in the microemulsion form. Furthermore, the viscosities of solutions of the spray-dried products tended to be significantly lower than desired.

Accordingly, there exists a need for a method of recovering water-soluble and

water-swellable polymers from dispersions, water-in-oil emulsions or water-in-oil microemulsions to produce rapidly dissolving water-soluble polymers without adversely affecting polymer properties. It would also be advantageous to provide blends of two or more spray-dried dry polymers and methods for production thereof wherein 90% or greater of the particles in the blend are each individually comprised of two or more polymers, so that the effect of stratification on the blend is minimized. There also exists a need for an economical method for producing substantially dry polymers having good handling and dissolution properties. It would also be advantageous to provide methods for spray-drying dispersions, water-in-oil emulsions and water-in-oil microemulsions which eliminate or reduce undesirable product changes, and enable component recycling or reuse.

A method has now been discovered for producing substantially dry water-soluble and water-swellable vinyl-addition polymers by spray-drying the corresponding polymer dispersion, water-in-oil emulsion, or water-in-oil microemulsion. Surprisingly, novel dry polymer products are obtained whose properties and/or performance are not detrimentally changed by the spray-drying process. Surprisingly, substantially dry polymers produced by methods of the instant invention tend to have improved stability relative to the corresponding dispersion, water-in-oil emulsion, or water-in-oil microemulsion polymers. Advantageous blends of two or more spray-dried dry polymers and methods for production thereof are also provided, wherein 90% or more of the particles in the blend are each individually comprised of two or more polymers. Surprisingly, the dissolution and handling characteristics of the spray-dried polymer particles of the instant invention are improved by agglomeration. Methods of using the instant compositions of polymer particles and agglomerates in water-treating, paper making, mining, oil, and agricultural industries are disclosed. In further embodiments of the invention, the oil phase of the water-in-oil emulsion or water-in-oil microemulsion is recovered, and purified in another embodiment, said oil phase being surprisingly substantially free of polymerization-debilitating substances.

Summary of the Invention

In one aspect the present invention provides polymer agglomerates comprised of porous polymer particles having at least one opening in their walls, wherein said agglomerates have a size in the range of about 120 to about 1500 microns, wherein at least about 5% of said agglomerates are larger than about 900 microns, and wherein said agglomerates are comprised of a water-soluble vinyl-addition polymer, or a crosslinked water-insoluble vinyl-addition polymer which would be water-soluble if not crosslinked, (i) having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt, or (ii) containing recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate.

In another aspect, there is provided a polymer composition comprised of (a) porous polymer particles having at least one opening in their walls and (b) polymer particles that do not have at least one opening in their walls, wherein said (a) and (b) are comprised of a water-soluble, acetone-insoluble, vinyl-addition polymer, or a crosslinked water-insoluble vinyl-addition polymer which would be water-soluble and acetone-insoluble if not crosslinked, (i) having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate,

sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt, or (ii) containing recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate, and wherein said (a) and (b) have a size in the range of about 200 microns to about 1200 microns.

The present invention also provides a method of treating suspended solids, comprising (a) intermixing the polymer agglomerates or polymer composition of the invention to form an aqueous mixture, (b) intermixing said aqueous mixture with suspended solids; and (c) separating resultant concentrated solids from resultant aqueous liquid.

According to the instant invention, there is also provided a process for producing substantially dry water-soluble or water-swellable vinyl-addition polymer particles

comprising (a) spray-drying a vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion into a gas stream with a residence time of about 8 to about 120 seconds and at an outlet temperature of about 70° C to less than 100° C and (b) collecting resultant polymer particles.

In another embodiment, there is provided a process for producing substantially dry water-soluble or water-swellable vinyl-addition polymer agglomerates comprising (a) spray-drying a vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion into a gas stream with a residence time of about 8 to about 120 seconds and at an outlet temperature of about 70° C to about 100° C, (b) collecting resultant polymer particles, and (c) agglomerating said polymer particles to form agglomerates.

In another embodiment, there is provided a process for producing substantially dry water-soluble or water-swellable polymer particles from a blend, comprising: (a) spray-drying a blend comprised of, or made by intermixing (i) a first water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion and (ii) a second water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion, into a gas stream with a residence time of about 8 to about 120 seconds and at an outlet temperature of about 70° C to about 150° C and (b) collecting resultant polymer particles.

In yet another embodiment, there is provided a process for producing substantially dry water-soluble or water-swellable polymer agglomerates from a blend, comprising: (A) spray-drying a blend comprised of, or made by intermixing, (I) a first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion and (II) a second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion, into a gas stream with a residence time of about 8 to about 120 seconds and at an outlet temperature of about 70° C to about 150° C, (B) collecting resultant polymer particles, and (C) agglomerating resultant polymer particles.

In another embodiment, there is provided a process for producing substantially dry water-soluble or water-swellable polymer agglomerates comprising (a) spray-drying a vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion (b) collecting resultant polymer particles; and (c) agglomerating said resultant polymer particles.

In yet another embodiment, there is provided a process for recovering oil from a water-soluble vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or

water-in-oil microemulsion spray-drying process, comprising (a) condensing spray-dry process-generated oil and water to obtain condensed oil and condensed water; and (b) separating said condensed oil from said condensed water, wherein said condensed oil is substantially free of non-gaseous polymerization-debilitating substances.

In still another embodiment, there is provided a process for purifying spray-dry process-generated oil, comprising (a) spray-drying a water-soluble vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion; (b) recovering spray-dry process-generated oil to obtain recovered oil; (c) intermixing said recovered oil with aqueous liquid to obtain purified oil; and (d) separating purified oil substantially free of non-gaseous polymerization-debilitating substances.

In a further embodiment, there is provided a process for purifying spray-dry process-generated oil, comprising (a) spray-drying a water-soluble vinyl-addition polymer-containing-containing water-in-oil emulsion or microemulsion into a gas stream with a residence time of about 8 to about 120 seconds and at an outlet temperature of about 70° C to about 120° C or at an outlet temperature of about 70° C to about 95° C; (b) collecting resultant polymer particles; (c) recovering spray-dry process-generated oil to obtain recovered oil; (d) intermixing said recovered oil with aqueous liquid to obtain purified oil; and (e) separating purified oil substantially free of non-gaseous polymerization-debilitating substances.

In a still further embodiment, there is provided substantially dry water-soluble or water-swellable polymer particles comprised of a functionalized polymer, or a polymer having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, hydroxamic acid salt, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate, said particles having a bulk density of about 0.4 grams per cubic centimeter to about 1.0 grams per cubic centimeter, as well as substantially dry water-soluble or water-swellable polymer agglomerates resulting from the agglomeration of these particles, and a method of treating suspended solids, comprising (a) dissolving, dispersing or intermixing substantially dry water-soluble or water-swellable polymer agglomerates with or in water to form a polymer solution, polymer dispersion, or aqueous mixture, (b) intermixing said polymer solution, dispersion or aqueous mixture with suspended solids, and (c) separating resultant concentrated solids from resultant aqueous liquid.

Finally, there are provided substantially dry water-soluble or water-swellable polymer

particles made by a process comprising (a) spray-drying a vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion into a gas stream with a particular residence time, preferably in the range of about 8 to about 120 seconds, and at a particular outlet temperature in the range of about 70° C to less than 100° C and (b) collecting resultant polymer particles, said polymer particles having a drying loss less than: (i) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion into a gas stream with a residence time of greater than about 120 seconds and at said particular outlet temperature and (b) collecting resultant polymer particles; or (ii) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion into a gas stream with said particular residence time and at an outlet temperature of greater than about 100°C and (b) collecting resultant polymer particles; or (iii) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion into a gas stream with a residence time of greater than about 120 seconds and at an outlet temperature of greater than about 100° C and (b) collecting resultant polymer particles, as well as substantially dry water-soluble or water-swellable polymer agglomerates resulting from the agglomeration of these particles, and a method of treating suspended solids, comprising (a) dissolving, dispersing or intermixing substantially dry water-soluble or water-swellable polymer agglomerates with or in water to form a polymer solution, polymer dispersion, or aqueous mixture, (b) intermixing said polymer solution, dispersion or aqueous mixture with suspended solids, and (c) separating resultant concentrated solids from resultant aqueous liquid

Detailed Description of the Preferred Embodiments

In accordance with the instant invention, vinyl-addition polymer-containing dispersions, water-in-oil emulsions, and water-in-oil microemulsions are sprayed-dried by a suitable means into a large chamber through which a hot gas is blown, thereby removing most or all of the volatiles and enabling the recovery of the dried polymer. Surprisingly, the means for spraying the dispersion, water-in-oil emulsion, or water-in-oil microemulsion into the gas stream are not particularly critical and are not limited to

pressure nozzles having specified orifice sizes; in fact, any known spray-drying apparatus may be used. For instance, means that are well known in the art such rotary atomizers, pressure nozzles, pneumatic nozzles, sonic nozzles, etc. can all be used to spray-dry the dispersion, water-in-oil emulsion, or water-in-oil microemulsion into the gas stream. The feed rate, feed viscosity, desired particle size of the spray-dried product, droplet size of the dispersion, water-in-oil emulsion, or water-in-oil microemulsion, etc. are factors which are typically considered when selecting the spraying means. The size and shape of the chamber, the number and type of spraying means, and other typical operational parameters may be selected to accommodate dryer conditions using common knowledge of those skilled in the art.

Although open cycle spray-dryers may be used, closed cycle spray-drying systems are preferred. Gas flow may be cocurrent, countercurrent or mixed flow, cocurrent flow being preferred. The hot gas, or inlet gas, may be any gas that does not react or form explosive mixtures with the feed and/or spray-dried polymer. Suitable gases used as the inlet gas are gases known to those skilled in the art, including air, nitrogen, and other gases which will not cause undesirable polymer degradation or contamination, preferably gases containing about 20% or less oxygen, more preferably about 15% or less oxygen. Most preferably, inert gases such as nitrogen, helium, etc. that contain about 5% or less of oxygen should be used.

The dried polymer may be collected by various means such as a simple outlet, classifying cone, bag filter, etc., or the polymer may be subjected to further stages of drying, such as by fluid beds, or agglomeration. The means for collecting the dry polymer product is not critical. The hot gas that remains after substantially all of the polymer is removed from the feed generally contains volatiles such as oil, water, etc. and may be vented to the atmosphere or recovered, preferably recovered and most preferably thereatter, recycled. The oil is generally recovered from a vinyl-addition polymer-containing dispersion, water-in-oil emulsion, and water-in-oil microemulsion spray-drying process by condensing spray-dry process-generated oil, preferably cocondensing spray-dry process-generated oil and spray-dry process-generated water, and separating condensed or recovered oil from condensed water. Said separating is easily accomplished by simply draining off the lower layer, and/or pumping off the upper layer, as water and oil are essentially immiscible. The difference in boiling points between water and oil may be such that the condenser may be operated at a temperature so as to only condense the oil, reducing the energy costs associated with condensing the vaporized water. However, it has been surprisingly discovered that

cocondensation of both the water and oil may be beneficial, as the recovered or cocondensed oil is generally substantially free of non-gaseous polymerization-debilitating substances. The volatiles are preferably condensed or cocondensed with a spray condenser. Spray condensers are well-known to those skilled in the art and function by spraying a liquid into hot gas, causing the hot gas to cool and causing the volatile oil, water, etc. contained in the hot gas to condense. The spray condenser may utilize an aqueous liquid, preferably water, more preferably aqueous acid, most preferably aqueous inorganic acid e.g. aqueous sulfuric acid. Polymerization-debilitating substances are those that inhibit or retard polymerization, or act as chain-transfer agents. Polymerization-debilitating chain-transfer agents may have chain transfer constants of about 10^{-4} or greater. Preferably, the condensed, cocondensed, or recovered oil contains less than about 0.1% of such polymerization-debilitating substances, more preferably less than about 0.05%, by weight based on total weight.

In some cases, recovered oil, which may be cocondensed or condensed oil, may not be as free of impurities or polymerization-debilitating substances as desired. Recovered oil may be purified by intermixing said recovered oil with aqueous liquid to obtain purified oil and separating said purified oil from the resultant aqueous liquid. Oil purified in this manner is typically substantially free of non-gaseous polymerization-debilitating substances, and is generally suitable for use in subsequent polymerizations. Said aqueous liquid is preferably water, more preferably aqueous acid. Said acid is preferably an inorganic acid, more preferably sulfuric acid. In a preferred embodiment, a vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion is comprised of an oil recovered from a polymer-containing water-in-oil emulsion or water-in-oil microemulsion spray-drying process. Both purified oil and recovered oil may be treated to remove gaseous polymerization-debilitating substances such as ammonia, oxygen, methylchloride, dimethylamine, formaldehyde, etc. by known means such as by sparging with an inert gas e.g. nitrogen, helium, etc.

One way to determine whether a treated, recovered, or purified oil is substantially free of non-gaseous polymerization-debilitating substances is to use a particular oil to prepare a vinyl-addition polymer-containing dispersion, water-in-oil emulsion, or water-in-oil microemulsion which is subsequently spray-dried, and then to recover the condensed or cocondensed oil and, optionally, to purify the recovered oil. If the resultant recovered or purified oil is substantially free of non-gaseous polymerization-debilitating substances, the molecular weight or solution viscosity of polyacrylamide prepared by polymerizing or copolymerizing acrylamide in a water-in-oil emulsion or water-in-oil microemulsion using

said particular oil will generally be substantially the same as the molecular weight or solution viscosity of polyacrylamide prepared by polymerizing acrylamide in a dispersion, water-in-oil emulsion or water-in-oil microemulsion using said recovered or purified oil, under otherwise substantially identical conditions.

In one embodiment of the instant invention, the level of formaldehyde in the recovered or purified oil obtained by spray-drying a dispersion, water-in-oil emulsion, or water-in-oil microemulsion, preferably a quaternized Mannich poly(alk)acrylamide microemulsion, is typically less than one hundred milligrams formaldehyde per kilogram of recovered or purified oil, preferably less than ten milligrams formaldehyde per kilogram of recovered or purified oil, and most preferably less than one milligram formaldehyde per kilogram of recovered or purified oil. Formaldehyde may be detrimental to certain types of polymerization processes, so that a very much reduced level of formaldehyde in the recovered or purified oil is a substantial advantage. It is economically and environmentally advantageous to recycle the oil for use in other processes, including the same or other polymerization processes. The lack of oil and certain residual chemical reagents from the post-reaction step, in particular formaldehyde, in the polymer particles are also substantial environmental advantages.

There are four interrelated operating parameters in the instant spray-drying process: gas inlet temperature, gas outlet temperature, product volatiles and residence time in the dryer. The outlet temperature generally should be about 150°C or below, preferably about 120°C or below, more preferably less than 100°C, even more preferably about 95°C or below, most preferably about 90°C or below. The outlet temperature is generally about 70°C or higher, preferably about 75°C or higher. Therefore, outlet temperatures are generally about 70° C to about 150° C, preferably about 70° C to about 120° C, more preferably about 70° C to less than 100°, even more preferably about 70° C to about 95° C, most preferably about 75°C to about 90°C. Outlet temperatures below about 70°C may be suitable in certain instances, though generally this is less preferred. For instance, at the cost of efficiency, spray drying could be carried out at long residence times, high gas flow rates and low outlet temperatures.

Generally, the dryer should be operated at the lowest possible outlet temperature consistent with obtaining a satisfactory product. To facilitate operating at the lowest possible operating temperature, the vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion is preferably comprised of a volatile oil. "Volatile", for purposes of this invention, means that the boiling point or upper end of the boiling point range of the oil is about 200°C or below, preferably about 190°C or below,

most preferably about 180°C or below. Although the use of an oil having a boiling point or upper end of the boiling point range of greater than 200°C may be acceptable in some cases, the use of a volatile oil allows for spray drying of the vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion to be carried out at low outlet temperatures so that polymer degradation is avoided or substantially reduced. Although in theory an oil with a very low boiling point, say room temperature or below, would be most preferable to avoid product degradation, in practice oils with low boiling points in this range may, under some circumstances, be unacceptable for other reasons related to handling and flammability. Thus, oils having a boiling point within the range from about 70°C to 190°C, preferably from about 130°C to about 185°C, most preferably from about 160°C to about 180°C are used. Suitable oils useful herein include any organic hydrocarbon liquids such as halogenated hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, mixtures of aromatic and aliphatic hydrocarbons, etc. usually containing about 6 to about 12 carbon atoms. Preferred examples of suitable hydrocarbons include perchloroethylene, benzene, xylene, toluene, mineral oil fractions, kerosenes, naphthas, petroleum fractions and the like. A most preferred oil is a material called Isopar* G manufactured by Exxon Chemical. Isopar G is a mixture of synthetic isoparaffinic hydrocarbons having a boiling point range of about 160°C to about 177°C.

The inlet temperature, the feed rate, and the composition of the polymer emulsion may all affect outlet temperatures. These parameters may be varied to provide a desired outlet temperature. Feed rates are not critical, and generally will vary depending on the size of the dryer and the gas flow rate. Inlet gas temperature is less critical than outlet gas temperature, and is generally about 140°C or above, preferably about 160°C or above. The inlet gas temperature is preferably about 200°C or below and more preferably about 180°C or below. Thus, preferred inlet gas temperature ranges from about 140°C to about 200°C, more preferably from about 160°C to about 180°C. Proper inlet gas temperatures tend to avoid product degradation on the high side and to avoid inadequate drying on the low side.

Residence time is a nominal value obtained by dividing the volume of the dryer by the volumetric gas flow. Residence time is generally at least about 8 seconds, preferably at least about 10 seconds. Residence time is generally no more than about 120 seconds, preferably no more than about 90 seconds, more preferably no more than about 60 seconds, and most preferably no more than about 30 seconds. Therefore, the general range of residence time is about 8 to about 120 seconds, preferably about 10 to

*Trade-mark

about 90 seconds, more preferably about 10 to about 60 seconds, and most preferably about 10 to about 30 seconds. It is known to those skilled in the art that longer residence times are to be expected when larger dryers are used or when the dryer is run in a less efficient manner. For instance, at the cost of efficiency, longer residence times would be expected at very low inlet temperatures and slow gas flow rates. As a practical matter, the residence times useful in the present invention may vary from the values described above, depending on the size and type of spray dryer used, the efficiency at which it is operated, and other operational parameters. Thus, residence times specified herein may be modified to accommodate dryer conditions using common knowledge of those skilled in the art.

Any water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion may be spray-dried by the processes of the instant invention. For purposes of this invention, water-swellable polymers are generally those that have been crosslinked to a certain degree, preferably by forming the polymer in the presence of certain amounts of crosslinking or branching agents. Preferably, water-swellable polymers include microbeads of U.S. Patent Nos. 5,274,055 and 5,167,766. Water-soluble, branched polymers generally result when smaller amounts of crosslinking agent are used to formulate the polymer, as in U.S. Patent Nos. 6,147,176 and 5,961,840. Most preferably, the water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion is as described in U. S. Pat. Nos. 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,286,806; 4,767,540; 5,274,055; 5,167,766; 5,847,056; 6,147,176; and 5,961,840. The vinyl-addition polymer content of the dispersion, water-in-oil emulsion or water-in-oil microemulsion is generally about 10% or greater, preferably greater than 15%, more preferably about 17% or greater, and most preferably 20% or greater, by weight based on total weight.

Preferably, vinyl-addition polymer-containing dispersions, water-in-oil emulsions or water-in-oil microemulsions are comprised of a polymer having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, hydroxamic acid salt, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate. Thus the polymer may be Mannich poly(alk)acrylamide, quaternized Mannich poly(alk)acrylamide, hydroxamated polyacrylamide, esterified (meth)acrylic acid polymer,

esterified (meth)acrylic acid copolymer, and hydrolyzed polyacrylamide. Hydrolyzed polyacrylamide may be formed by inadvertent hydrolysis during production, but is preferably post-reacted e.g. deliberately reacted with acid or base to a degree of hydrolysis of 5 mole% or more, preferably 10 mole% or more, based on total moles of recurring units, most preferably as disclosed in U.S. Patent No. 5,286,806. The polymer may contain recurring units selected from the group consisting of acrylamide, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, quaternized dialkylaminoalkyl(alk)acrylate, (meth)acrylic acid, and salts of (meth)acrylic acid. Preferred polymers included (1) a polymer containing 10 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and having a standard viscosity of at least about 8.0 cps, (2) a polymer containing 20 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and having a standard viscosity of at least about 9.0 cps, (3) a polymer containing at least about 1 mole % of tertiary aminomethyl groups, (4) an acrylamide polymer containing at least about 1 mole% of quaternized tertiary aminomethyl groups, (5) an acrylamide polymer containing at least about 1 mole% of hydroxamic acid or hydroxamic acid salt groups, (6) an esterified polymer containing hydroxamic acid groups and carboxylic acid groups or salts thereof, and (7) an ionic, organic, polymer microbead being less than about 750 nanometers in diameter if crosslinked and less than about 60 nanometers in diameter if non-crosslinked and water-insoluble, the ionicity of the microbead being at least about 1%, preferably having 1 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt. Polymers and copolymers of acrylamide are particularly preferred.

In a preferred embodiment, the vinyl-addition polymer-containing water-in-oil emulsion or microemulsion is a Mannich poly(alk)acrylamide- or quaternized Mannich poly(alk)acrylamide-containing water-in-oil emulsion or microemulsion. Mannich polyacrylamide and quaternary Mannich polyacrylamide water-in-oil microemulsions may be heat treated prior to spray drying according to methods described in U.S. Patent No. 5,627,260.

The instant invention is of particular value for preparing substantially dry, functionalized or post-reacted polymers. In many cases functionalized polymers are those that may be or have been post-reacted, e.g. a chemical reaction has been performed on the polymer after the formation of the polymer from the corresponding

monomers, see e.g. U.S. Patent No. 4,956,400. The chemical reaction is generally deliberate or purposeful, and polymers which are inadvertently or indifferently reacted e.g. slightly hydrolyzed during the course of production are not generally considered to be functionalized. For example, Mannich poly(alk)acrylamides, quaternized Mannich poly(alk)acrylamides, acid- or base- hydrolyzed polyacrylamides, hydroxamated poly(alk)acrylamides, etc. are functionalized polymers that are difficult or impossible to prepare in solution or gel form. Since the usual means of preparing dry polymers is via a gel or solution polymerization as described above, dispersion, water-in-oil emulsion and water-in-oil microemulsion may be the only practical method for the preparation of functionalized or postreacted polymers.

The water-soluble or water-swellable vinyl-addition polymer-containing dispersions, water-in-oil emulsions or water-in-oil microemulsions of the instant invention are generally prepared by polymerization of the corresponding monomers, preferably as described in U. S. Pat. Nos. 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,286,806; 4,767,540; 5,274,055; 5,167,766; 5,847,056; 6,147,176; and 5,961,840. The monomers may be polymerized in a dispersion, water-in-oil emulsion or water-in-oil microemulsion; water-in-oil emulsion or water-in-oil microemulsion are preferred. All dispersions, emulsions and microemulsions described herein are inverse or water-in-oil. An emulsion, for purposes of this invention, is generally defined as a composition comprising two liquids or phases which are insoluble in each other along with a surfactant, surfactant mixture or emulsifier. A microemulsion, for purposes of this invention, is generally defined as a thermodynamically stable composition comprising two liquids or phases which are insoluble in each other along with a surfactant, surfactant mixture or emulsifier. Polymeric inverse microemulsions which contain a continuous oil phase and a polymer-containing discontinuous phase (usually aqueous) are prepared from thermodynamically stable monomer microemulsions. Inverse microemulsions have a narrow droplet size distribution and are usually, but not always, optically transparent. The discontinuous polymer-containing phase of a microemulsion forms droplets or micelles, which are usually aqueous and usually have a volume average droplet diameter which is less than about 2500 Å, preferably less than about 2000 Å, and most preferably less than about 1000 Å. Some microemulsions may have a volume average droplet diameter as large as about 3000 Å.

Water-in-oil emulsions are well-known in the art, see e.g. Vanderhoff U.S. Patent No. 3,284,393. For the purposes of this invention, dispersions are compositions

comprised of polymer beads or droplets that are dispersed in a non-aqueous liquid e.g. oil, generally with reduced surfactant levels, but generally including other types of stabilizers, as described in e.g. U.S. Patent Nos. 4,528,321; 4,628,078; and 4,506,062.

Homopolymers and copolymers of the monomers enumerated herein are fully encompassed by the instant invention. Preferred nonionic monomers are water-soluble monomers such as (meth)acrylamide, N-vinyl pyrrolidone, N,N-dialkyl(meth)acrylamide, hydroxyalkyl(meth)acrylate, N-vinylformamide and the like. Small quantities e.g. about 10% or less, of other monomers having limited water solubility e.g. methyl acrylate, styrene, methyl methacrylate, acrylonitrile, vinyl acetate, etc. may also be used, provided that the resulting polymer is water-soluble or water-swellable. Generally, water-swellable polymers are crosslinked polymers, not polymers containing so many water-insoluble recurring units that they swell without dissolving in water. Acrylamide and methacrylamide are especially preferred non-ionic monomers. Although, in some instances, the polymer may contain 80% or even 100% nonionic monomer, preferably, the polymer contains about 50% or less of nonionic monomer, preferably about 40% or less, most preferably about 30% or less, by mole based on total moles of polymer repeat units. Water-swellable polymers or water-soluble, branched polymers may be produced by copolymerization with multifunctional branching agents e.g. methylenebisacrylamide.

Useful cationic monomers include salts and quaternaries of dialkylaminoalkyl(alk)acrylate and dialkylaminoalkyl(meth)acrylamide, and diallyldialkylammonium halide. Preferred quaternizing agents are methyl chloride, ethyl chloride, benzyl chloride, dimethylsulfate, and diethylsulfate. Preferred cationic monomers include the methyl chloride salt of dimethylaminoethyl(meth)acrylate, the methyl chloride salt of dimethylaminopropyl(meth)acrylamide, and diallyldimethylammonium chloride. Preferably, the polymer contains about 5% or more of cationic monomer, preferably about 10% or more, most preferably about 30% or more, by mole based on total moles of polymer repeat units.

Useful anionic monomers include (meth)acrylic acid, fumaric acid, crotonic acid, maleic acid, 2-acrylamido-2-methylpropanesulfonic acid, styrenesulfonic acid, and salts thereof. Sodium and ammonium salts are preferred. Preferred anionic monomers include sodium acrylate, potassium acrylate, ammonium acrylate, and the sodium salt of 2-acrylamido-2-methylpropanesulfonic acid. Generally, the polymers contain enough of the salt form of the acid such that the polymer is water-soluble or water-swellable, preferably greater than 50% of the acid monomers are in the salt form, more preferably

60% or greater, by weight based on total weight. Preferably, the polymer contains about 5% or more of anionic monomer, preferably about 50% or more, more preferably about 70% or more, most preferably about 75% or more, by mole based on total moles of polymer repeat units.

The polymerization may be carried out in the presence of such conventional additives as are desired. For example, the polymerization may contain chelating agents to remove polymerization inhibitors, chain transfer agents, pH adjusters, initiators and other conventional additives. Polymerization of the monomers may be carried out in any manner known to those skilled in the art. Initiation may be effected with a variety of thermal and redox free radical initiators, including peroxides, e.g. t-butyl peroxide; azo compounds, e.g. azobisisobutyronitrile; inorganic compounds, such as potassium persulfate and redox couples, such as ferrous ammonium sulfate/ammonium persulfate. A preferred initiator is sodium bromate/sulfur dioxide. Initiator addition may be effected any time prior to the actual polymerization per se. Polymerization may also be effected by photochemical irradiation processes, such as ultraviolet irradiation or by ionizing irradiation from a cobalt 60 source.

Surfactants and/or dispersing agents are generally helpful and sometimes necessary for the formation and continued stability of vinyl-addition polymer-containing dispersions, water-in-oil emulsions and water-in-oil microemulsions. Where spray-drying is contemplated, ongoing stability may not be required, and it may be advantageous to reduce or eliminate the surfactants and/or dispersing agents. Vinyl-addition polymer-containing dispersions, water-in-oil emulsions and water-in-oil microemulsions may be prepared using little or no surfactants and/or dispersing agent and spray-dried soon thereafter, preferably during the period of continued stability. Preferably, the vinyl-addition polymer-containing dispersions, water-in-oil emulsions and water-in-oil microemulsions contain about 2% or less of surfactant and/or dispersing agent, more preferably about 1% or less, by weight based on total weight. The spray-dried polymer particles made by the processes of instant invention preferably contain 6% or less of surfactant and/or dispersing agent, preferably 4% or less.

Substantially dry water-soluble or water-swellable polymer particles may be produced from a blend by (a) spray-drying a blend comprised of, or made by intermixing, (i) a first water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion and (ii) a second water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion, and (b) collecting resultant polymer particles. Preferred

blends of water-in-oil emulsions and water-in-oil microemulsions are disclosed in U.S. Patent Nos. 5,914,366; 5,763,530; and 5,763,523.

Blending of water-in-oil emulsions and water-in-oil microemulsions may advantageously provide a product with improved performance by e.g. providing a property such as charge or molecular weight that is different from the individual emulsions or microemulsions from which the blend is derived. The different property may result from averaging of the properties of the blend components, or occasionally synergistic results may be observed. For instance, when treating substrates that are themselves blends or mixtures of various components, each of the blend components may have a specific role in product performance. Accordingly, although two identical water-in-oil emulsions and water-in-oil microemulsions could be blended, it it generally preferred to blend emulsions or microemulsions that are different from each other e.g. *different performance, different charge, different viscosity, different molecular weight,* different physical form, different chemical identity, different aging characteristics, different costs, etc.

Spray-drying of blends is advantageous because typically 90% or greater, preferably 95% or greater, most preferably substantially all, of the resultant spray-dried polymer particles each individually contains two or more water-soluble or water-swellable vinyl-addition polymers, so that stratification effects may be minimized. Spray-drying a blend may be particularly advantageous when the first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion has a viscosity that is different from the viscosity of the second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion. This is because viscosity generally impacts the particle size distribution of the spray dried polymer particles, so that the particle size distribution of the particles obtained from the first water-in-oil emulsion or water-in-oil microemulsion may be different from the particle size distribution of the particles obtained from the second water-in-oil emulsion or water-in-oil microemulsion. A dry blend of the two different polymers is thus likely to exhibit greater stratification than a dry blend obtained by spray-drying a blend of the first and second water-in-oil emulsions or water-in-oil microemulsions.

In another embodiment of the instant invention, the Mannich and quaternary Mannich polymer particles have, in some cases, substantially reduced residual contamination by certain chemical reagents added during the functionalization step e.g. formaldehyde, methyl chloride and amines. Typically, the residual level of methyl

chloride in the polymer particles is below 500 parts per million parts (ppm), based on the total weight of the particles, and preferably below 100 ppm, same basis. Formaldehyde is typically below 2000 ppm and preferably below 1000 ppm, same basis. Individual residual amines, which may be present as their hydrochloride salts, are typically present at below 20,000 ppm and preferably below 10,000 ppm, same basis.

With respect to the various spray-dried and agglomerated polymer products described herein, the optimum standard viscosity for a particular polymer is very dependent on the application e.g. flocculation of suspended solids, paper making, oil recovery, mining, etc. For instance, for many applications, it is preferred that the standard viscosity of the polymer particles be about 1.5 centipoise or greater, more preferably about 2.0 centipoise or greater., most preferably about 2.5 centipoise or greater. However, applications other than flocculation may require polymers with standard viscosities higher or lower than those given above. One advantage of the instant invention is that the standard viscosity of the polymer particles produced according to the processes described herein is generally within about 15% of the standard viscosity of the corresponding polymer dispersion, water-in-oil emulsion or water-in-oil microemulsion. This indicates that the polymers are not substantially altered by the spray-drying process.

Generally, the polymers of the instant invention have a molecular weight of about 100,000 or greater, preferably greater than about 1,000,000; more preferably greater than about 10,000,000, most preferably greater than about 20,000,000. The optimum molecular weight or molecular weight range for a particular polymer is also very dependent on the application e.g. flocculation of suspended solids, paper making, oil recovery, mining, etc. For instance, for many flocculant applications, Mannich polyacrylamide and quatemized derivatives thereof have a molecular weight greater than about 100,000 and preferably greater than about 1,000,000. However, applications other than flocculation may require polymers with molecular weights higher or lower than those given above. The water-soluble polymers produced by the processes described herein may contain small amounts of insoluble polymer. Such small amounts of insoluble polymer do not generally affect the performance of the polymer in, for instance, the applications mentioned above. In some cases, water-swellable polymers are desired for applications such as fluid thickening, papermaking, printing ink thickeners, etc.

When produced according to the spray drying processes disclosed herein, polymer particles of the instant invention are generally about 10 microns or greater in diameter, preferably about 40 microns or greater, more preferably about 100 microns or greater,

most preferably about 200 microns or greater. It is preferred that the polymer particles be non-dusting. Dusting and flow problems are typically exacerbated when the polymer particles are small, so larger polymer particles are generally desirable. However, very large particles may dissolve more slowly. Therefore, it is generally desirable for the polymer particles to be about 1200 microns or less in diameter, preferably about 800 microns or less in diameter, more preferably about 600 microns or less, most preferably about 400 microns or less. Generally, at least about 90% of the polymer particles range in size from about 10 microns to about 1200 microns, preferably at least about 95%, more preferably at least about 98%. The size of the polymer particles can be varied somewhat by altering the operational parameters e.g. spray configuration, emulsion viscosity, feed rate, etc. Particles may be substantially spherical or non-spherical; "diameter" of a non-spherical particle is the dimension along a major axis.

Although in some cases the particles are hollow, porous structures having at least one opening in their walls, it has been discovered that these features are not always necessary in order to obtain particles having desirable properties e.g. fast dissolution times. In many cases, the spray-drying parameters e.g. nozzle type, nozzle size, outlet temperature, etc. needed to produce particles that are hollow, porous structures having at least one opening in their walls are inconvenient or uneconomical, and it is advantageous to produce particles that lack some or all of these features.

The particles formed by the spray-drying processes of the instant invention may be screened to remove an oversize or undersize fraction. Oversize particles may be fragmented by e.g. grinding, whereas undersized particles are generally agglomerated. Sizes may be determined by methods known to those skilled in the art e.g. sieving, screening, light scattering, microscopy, microscopic automated image analysis, etc.

Surprisingly, the bulk densities of the spray-dried polymer particles of the instant invention are generally greater than the bulk densities of dry polymers prepared by precipitation of the corresponding dispersion, water-in-oil emulsion or water-in-oil microemulsion. Polymer particles having greater density may be advantageous because they occupy a smaller volume, resulting in e.g. lower shipping and storage costs. Whereas the densities of precipitated polymers are usually less than about 0.35 grams per cubic centimeter (g/cc), the bulk densities of the spray-dried polymer particles of the instant invention are generally about 0.35 g/cc or greater, preferably about 0.4 g/cc or greater, more preferably about 0.45 g/cc or greater, most preferably about 0.50 g/cc or greater. The bulk densities of the spray-dried polymer particles of the instant invention are generally about 1.1 g/cc or less, preferably about 1.0 g/cc or less, more preferably

about 0.95 g/cc or less, most preferably about 0.90 g/cc or less. Therefore, the bulk densities of the spray-dried polymer particles of the instant invention generally range from about 0.35 to about 1.1 g/cc, preferably about 0.4 to about 1.0 g/cc, more preferably about 0.45 to about 0.95 g/cc, most preferably about 0.50 to about 0.90 g/cc.

Under the conditions of drying set forth herein, the polymer particles produced by the processes described herein are substantially dry. As used to describe the polymer produced herein, "substantially dry" generally means that the polymer contains about 12% or less volatiles, preferably about 10% or less by weight, based on the weight of the spray dried polymer. The polymer generally contains about 2% or more volatiles, preferably about 5% or more, by weight based on total weight, and most preferably contains from about 8% to about 10% volatiles by weight, same basis. The volatiles are measured by determining the weight loss on drying the polymer product at about 105°C for about 30 minutes.

Substantially dry water-soluble or water-swellable polymer particles of the instant invention may be made by a process comprising (a) spray-drying a vinyl-addition polymer-containing water-in-oil dispersion, emulsion or water-in-oil microemulsion into a gas stream with a particular residence time, preferably in the range of about 8 to about 120 seconds, and at a particular outlet temperature in the range of about 70° C to less than about 100° C and (b) collecting resultant polymer particles. These polymer particles are encompassed within the instant invention when they have a drying loss less than: (i) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion into a gas stream with a residence time of greater than about 120 seconds and at said particular outlet temperature and (b) collecting resultant polymer particles; or (ii) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion into a gas stream with said particular residence time and at an outlet temperature of greater than about 100° C and (b) collecting resultant polymer particles; or (iii) the drying loss of substantially dry water-soluble or water-swellable polymer particles made by a process comprising (a) spray-drying said vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion into a gas stream with a residence time of greater than about 120 seconds and at an outlet temperature of greater than about 100° C and (b) collecting resultant polymer particles. As used herein, "drying loss" is the change in polymer

viscosity resulting from spray-drying, and is not to be confused with "loss on drying," or LOD, which is a measure of volatiles as described in the Examples. Drying loss may be expressed as the viscosity before spray drying minus the viscosity after spray drying, divided by the viscosity before spray drying, and expressed as a percentage by multiplying by 100.

Additional materials such as flow control agents, dust control agents, pH adjusting agents, surfactant, emulsifier, etc. and the like may be added to the emulsion or microemulsion before or during the spray drying process, or to the polymer particles after the spray drying process, or both, to enhance the production, distribution, packaging, handling, performance, etc. and the like of the polymer particles.

We have also discovered that mixing, in any order, an acid, base or buffer with the substantially dry water-soluble polymer particles that are the product of the spray drying processes described herein, may be advantageous. A buffer, for the purposes of this invention, is a substance or blend of substances that, when dissolved in water, gives a solution that resists changes in pH when small amounts of acid or base are added. Preferably, a buffer contains an acid and a base. For example, any solution of a weak acid plus a salt of that acid is a buffer solution. A base, for the purposes of this invention, is a substance or blend of substances that, when dissolved in pure water, gives a solution with a pH value greater than 7. An acid, for the purposes of this invention, is a substance or blend of substances that, when dissolved in pure water, gives a solution with a pH value less than 7. The addition of an acid, base or buffer to the polymer particles may enhance the flow properties of the dry polymer particles and adjusts the pH of the solution that the polymer particles are dissolved into so as to enhance the rate of dissolution and performance of the polymer particles in the desired application. Bases are preferred and buffers are most preferred. Acids, bases and buffers useful in the instant invention may be solid or liquid, though it is especially preferred to use an acid, base, or buffer that is substantially dry so as to avoid clumping. Substantially dry, when used to describe the acid, base, or buffer for the purposes of this invention, means that the powdered acid, base, or buffer flows freely. The acid, base, or buffer may be hydrated as long as it flows freely.

Any base known in the art may be used. Suitable powdered bases may include the alkali and alkaline earth metal salts of carbonate, bicarbonate, citrate, phosphate and acetate. Preferred bases may include sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium acetate, potassium acetate, sodium citrate, potassium citrate, sodium phosphate, potassium phosphate, etc. and the

like. Sodium carbonate and sodium bicarbonate are more preferred, and sodium bicarbonate is most preferred. The mixture of the base and the polymer particles is such that the base may be incorporated into the interior of the particles, or may coat the surface of the particles, or may be distinct from the particles, or any combination thereof.

Any buffer known in the art may be used. Suitable buffers may comprise the alkali and alkaline earth metal salts of carbonate, bicarbonate, citrate, phosphate and acetate, with the corresponding acid. The mixture of the buffer and the polymer particles is such that the base may be incorporated into the interior of the particles, or may coat the surface of the particles, or may be distinct from the particles, or any combination thereof. The buffer system KH_2PO_4 / Na_2HPO_4 or hydrates thereof is most preferred.

Any acid known in the art may be used. Suitable acids may comprise inorganic acids e.g. hydrochloric acid, nitrous acid, nitric acid, carbonic acid, phosphoric acid, phosphorus acid, sulfurous acid, and sulfuric acid, as well as organic acids e.g. acetic acid, lactic acid, citric acid, formic acid, alkylsulfonic acids, etc. and the like. Acids such as KH_2PO_4, NAH_2PO_4 and hydrates thereof are preferred. In instances where a quaternary Mannich polyacrylamide microemulsion is heat treated by, for example, adjusting the pH to about 3.6 to about 4.8 adding formaldehyde scavenger, adjusting the water content to about 10-45 weight percent of polymer and heating the resultant emulsion at from about 40°C to about 80°C for about 3 to about 20 hours, the acid is preferably added in addition to and after the heat treating step.

It is preferred to add the acid, base or buffer directly to the polymer particles. Alternatively, and less preferably, an acid, base or buffer may be dissolved in water or oil to form a solution or slurry and added to the water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion before spray drying. The solution or slurry of the acid, base or buffer may be spray dried simultaneously or substantially simultaneously with the spray drying of the water-in-oil emulsion or water-in-oil microemulsion, or the acid, base, or buffer may be added directly to the spray dryer while simultaneously or substantially simultaneously spray drying the water-in-oil emulsion or water-in-oil microemulsion, to form polymer particles which comprise the acid, base, or buffer. In this case, the acid, base, or buffer need not be substantially dry. Another, also less preferred, way to add one or more acids, bases, or buffers to the polymer is to add part of the acid, base, or buffer before or during the spray dry process, and part of the acid, base, or buffer, or perhaps a different acid, base, or buffer, to the resulting polymer particles. The buffer may be formed when a base is added to an water-in-oil emulsion or water-in-oil microemulsion

or polymer particle which already contains the corresponding acid, or the buffer may be formed when an acid is added to a water-in-oil emulsion or water-in-oil microemulsion or polymer particle that already contains the corresponding base.

The amount of acid, base or buffer to be added to the water-soluble Mannich acrylamide or quaternized Mannich acrylamide polymer particles of the present invention is preferably an amount sufficient to provide a solution pH of from about 5 to about 11, preferably from about 5.5 to about 9 and most preferably about 6 to about 8, when the particles or particle compositions are dissolved in water. Regardless of the manner in which acid, base or buffer is added (i.e., whether added to the emulsion prior to or during spray drying or to the particles after spray drying) the amount should be such that the resulting solution containing dissolved polymer particles has a pH at least about 5, preferably at least about 6 and below about 11, preferably a pH below about 8.

It is understood that the pH of the resulting solution will depend on the pH of the water before the polymer particles are added. For instance, in order to produce a preferred pH in the resulting solution in the range of about 5 to about 9, more base should generally be present in the particles if the water is more acidic than if the water is less acidic. It is likewise understood that the preferred amount of base present in the polymer particles may depend on the pH of the water into which the polymer particles are to be dissolved. For example, for many waters of moderate acidity, the polymer particles should contain about 0.1% to about 3.5%, based on total weight, of a preferred base such as sodium bicarbonate. Generally, the polymer particles may contain base in an amount of at least about 0.05% by weight, preferably at least about 0.1% and generally up to about 10.0% preferably up to about 20.0% by weight based on total particle weight. More preferably the amount of base ranges from about 0.05% to about 5.0%, based on total weight of particles. The aforesaid amounts also apply to acids. Similar reasoning is understood concerning the optimum amount of acid; i.e. the presence of more acid will be preferred in the particles when the water is more basic than when the water is less basic in order for the solution of the polymer to have the desired pH. Routine experimentation by one skilled in the art may be used to determine the appropriate amount of acid, base or buffer for a particular water.

Likewise, the amount of buffer will also depend on the pH of the water before the polymer particles are added. The amount of buffer present will tend to affect the ability of the polymer solution to resist changes in pH. For instance, for a preferred buffer system such as KH_2PO_4 / $Na_2HPO_4 \cdot 12\ H_20$, the buffer should be at least about 0.1%, by weight, and preferably at least about 5%, by weight, of the total weight of the

particles. Although it would seem preferable to use as much buffer as possible so as to provide the polymer solution with the greatest ability to resist pH changes, it is also preferable for the polymer particles to contain as much polymer as possible. Thus, in practice, the buffer should comprise less than 50%, by weight, of the polymer particles, and preferably less than 30%, by weight, same basis. Therefore, the buffer should be present in the polymer particles at a level of at least about .05%, generally from about 0.1% to about 50%, by weight, and preferably about 5% to about 30%, by weight, based on the total particle weight. The exact amount of buffer depends on the pH of the water and how strongly the polymer solution needs to be able to resist changes in pH.

In addition to pH, another factor which tends to influence the rate of dissolution of the polymer particles and the performance of the polymer is the temperature of the polymer solution or the solution into which the polymer particles are dissolved. Therefore, the amount of acid, base, or buffer present in the polymer particles may vary depending on the temperature of the water into which the polymer is to be dissolved. For instance, quaternized Mannich polyacrylamide tends to dissolve more readily at higher temperatures, so that a lower pH, such as about 5, may be desired to dissolve the polymer when the temperature of the water is higher, such as about 35°C, whereas a pH of about 8 may be preferred if the water temperature is very low, such as about 5°C. It is apparent, therefore, from the foregoing that less base, or more acid, might be preferred at high temperatures than at low temperatures, and that the selection of buffer will also depend on the temperature.

The particle size of the acid, base, or buffer is not particularly important, and may be varied to optimize the flow properties of the mixture with the polymer particles. For instance, a preferred range of particle sizes for sodium bicarbonate is from about 10 to about 500 microns, more preferably about 50 to about 300 microns. The means for adding and mixing the substantially dry base to the polymer particles are likewise not critical. Any mechanical mixing means known to those skilled in the art for mixing granular solids is suitable.

It has also been discovered that agglomeration of the polymer particles of the instant invention may improve the flow properties and dissolution times of the polymers. Agglomeration is a known process for increasing particle size and various methods for agglomerating particles are known to those skilled in the art, e.g. "Successfully Use Agglomeration for Size Enlargement," by Wolfgang Pietsch, Chemical Engineering Progress, April 1996, pp. 29-45; "Speeding up Continuous Mixing Agglomeration with Fast Agitation and Short Residence Times," by Peter Koenig, Powder and Bulk

Engineering, February 1996, pp. 67-84. Known agglomeration methods such as natural agglomeration, mechanical agglomeration, tumble or growth agglomeration, pressure agglomeration, binderless agglomeration, agglomeration with binders, etc., may be used to agglomerate the polymer particles of the instant invention. Agglomeration may optionally be followed by drying, e.g. fluid bed drying, to remove binder, e.g. water. Pressure agglomeration is preferred, and mechanical agglomeration using a water binder, followed by fluid bed drying is most preferred.

The agglomerates formed by agglomerating the polymer particles of the instant invention tend to have improved flow properties and faster dissolution times when compared to the unagglomerated polymer particles. Preferably, the agglomerates are non-dusting. Flow properties may be measured by measuring flow times as described in the Examples. Dissolution rates may be determined by measuring the increase in viscosity of a polymer solution as a function of dissolution time, as described in the Examples. Typically, about 90% of the agglomerates of the instant invention have an agglomerate size of about 120 microns or greater, preferably about 160 microns or greater, more preferably about 200 microns or greater, most preferably about 300 microns or greater. Generally, about 90% of the agglomerates have an agglomerate size of about 1500 microns or less, preferably about 1200 microns or less, more preferably about 1100 microns or less, most preferably about 1000 microns or less. Thus, about 90%, preferably 95%, of the agglomerates have a size in the range of about 120 to about 1500 microns, preferably about 160 microns to about 1200 microns, more preferably about 200 microns to about 1100 microns, most preferably about 300 microns to about 1000 microns Usually, at least about 5% of the agglomerates, preferably at least about 10%, most preferably at least about 15%, are larger than about 900 microns. The agglomerates formed by agglomerating the spray-dried particles of the instant invention may be screened to remove an oversize or undersize fraction. Preferably, agglomerates larger than about 1200 microns and smaller than about 175 microns are removed by e.g. screening. Oversize agglomerates are generally fragmented by e.g. grinding, whereas undersized agglomerates are generally recycled into the agglomerator.

The bulk density values of the agglomerates of the instant invention tend to be lower than the bulk density values of the spray-dried particles from which they are formed. The bulk densities of the agglomerates of the instant invention are generally about 0.35 g/cc or greater, preferably about 0.4 g/cc or greater, more preferably about 0.45 g/cc or greater, most preferably about 0.50 g/cc or greater. The bulk densities of

the agglomerates of the instant invention are generally about 1.0 g/cc or less, preferably about 0.95 g/cc or less, more preferably about 0.90 g/cc or less, most preferably about 0.85 g/cc or less. Therefore, the bulk densities of the agglomerates of the instant invention generally range from about 0.35 to about 1.0 g/cc, preferably about 0.4 to about 0.95 g/cc, more preferably about 0.45 to about 0.90 g/cc, most preferably about 0.50 to about 0.85 g/cc.

In order to obtain agglomerates of a preferred size, it is preferred that the polymer particles themselves be of such a size that they are agglomerable. Agglomeration obviously tends to multiply the average particle size, so that it is frequently easier to cause large increases in particle size than it is to cause small increases in particle size. Therefore, to produce agglomerates of a preferred size or size range, it is generally preferred to agglomerate particles that are much smaller than the desired agglomerate size, rather than particles that are only slightly smaller. Agglomerable particles are generally those that may be conveniently agglomerated to produce agglomerates having a preffered size. It is possible, but less preferred, to agglomerate larger particles to produce agglomerates that are larger than desired, then remove the oversize agglomerates as described above.

The substantially dry polymer particles and agglomerates of the present invention are generally comprised of the polymer that was contained in the dispersion, water-in-oil emulsion, or water-in-oil microemulsion that was spray-dried, as discussed hereinabove. Preferably, the substantially dry polymer particles and agglomerates of the present invention are comprised of polymer having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, hydroxamic acid salt, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate. Polymers and copolymers of acrylamide are preferred.

In a preferred embodiment, substantially dry water-soluble or water-swellable polymer particles and agglomerates are comprised of a polymer having 1 mole % or more of recurring units having pendant groups selected from the group consisting of tertiary aminomethyl, quaternized tertiary aminomethyl, glyoxal, hydroxamic acid, and hydroxamic acid salt, based on total moles of recurring units. In another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of a polymer having 1 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt,

based on total moles of recurring units, said polymer having a standard viscosity of about 7.0 cps or greater, and in another preferred embodiment, said polymer is further comprised of recurring units having pendant alkyl ester groups, wherein said alkyl ester groups contain from about 2 to about 12 carbon atoms. In another preferred embodiment, substantially dry water-soluble or water-swellable polymer particles and agglomerates are comprised of acrylamide, (meth)acryloxyethyltrimethylammonium chloride, copolymers thereof, and, optionally, branching agent e.g. methylenebisacrylamide, as described in U.S. Patent Nos. 6,147,176 and 5,961,840.

In another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of a polymer having 10 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and wherein said polymer has a standard viscosity of at least about 8.0 cps, or (b) wherein said polymer contains 20 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and wherein said polymer has a standard viscosity of at least about 9.0 cps.

In yet another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of an ionic, organic, polymer microbead being less than about 750 nanometers in diameter if crosslinked and less than about 60 nanometers in diameter if non-crosslinked and water-insoluble, the ionicity of the microbead being at least about 1%.

The substantially dry polymer particles and agglomerates of the present invention generally exhibit improved stability relative to the dispersion, water-in-oil emulsion, or water-in-oil microemulsion from which they were derived. For instance, Table 7 shows the change in standard viscosity as a function of time at 90°C for spray dried quaternized Mannich polyacrylamide, compared to a quaternized Mannich polyacrylamide microemulsion from which the spray dried polymer was derived. The standard viscosity of the microemulsion polymer changed substantially as a function of time, whereas the change in standard viscosity for the spray dried polymer was much less. Table 8 shows data obtained in a similar manner, except that the dry polymer and the microemulsion polymer were stored at ambient temperature. Once again, the standard viscosity of the microemulsion polymer changed substantially as a function of time, whereas the change in standard viscosity for the spray dried polymer was not substantial. In both cases, at room temperature and at 90°C, it is quite surprising that

the spray dried polymer shows greater stability, as measured by standard viscosity, than the corresponding polymer contained in the microemulsion.

Surprisingly, the standard viscosities of the polymer particles and agglomerates that are the product of the process described herein are not substantially reduced by the spray drying process of the invention. Generally, the standard viscosity values of the polymer particles are not decreased by greater than about 15 % of their initial value, preferably not greater than about 10%, more preferably not greater than about 8%, most preferably not greater than about 5%, as a result of the spray drying process, even when the standard viscosity of the polymer in the polymer-containing water-in-oil microemulsions is observed to decrease quickly at elevated temperatures as described hereinabove. It is also surprising that the short residence times result in polymer particles with low volatile levels. Moreover, the residual level of oil in the finely divided polymer particles is typically very low, usually less than 1.0 % by weight, based on the total weight of the particles, and preferably less than 0.2% by weight, same basis.

The free flowing, substantially dry, water-soluble polymer particles and agglomerates that are the product of the invention described herein may be used in many applications, such as, for example, solids/liquids separation; flocculants for mining operations to recover ore from slurries; flocculants for water treating to remove suspended impurities etc.; in paper making as a flocculant and to aid paper formation e.g. retention aids; in oil recovery industries e.g enhanced oil recovery, treatment of oily wastewater, etc.; in agriculture e.g. soil stabilization or soil conditioning; in biotechnological applications e.g. treatment of enzyme broths; and in food processing e.g. flocculation of suspended food particles. The polymers of the present invention can conveniently be employed e.g. as flocculants in the form of dilute aqueous solutions. These solutions can be prepared by intermixing, dispersing, and/or dissolving the particles in or with water. Concentrating dispersions of suspended solids is carried out by adding an effective amount of the dilute aqueous solution to the suspension to produce an effluent of desired characteristics. For instance, a preferred method of treating suspended solids comprises (a) dissolving, dispersing, or intermixing substantially dry water-soluble or water-swellable polymer particles or agglomerates in or with water to form a polymer solution, polymer dispersion, or aqueous mixture, (b) intermixing said polymer solution, dispersion or aqueous mixture with suspended solids, and (c) separating resultant concentrated solids from resultant aqueous liquid.

The polymer products of this invention are useful in a wide range of solid-liquid separations. These polymers may be used in the dewatering of biologically treated

suspensions, such as sewage or other municipal and industrial sludges, the drainage of cellulosic suspension such as those found in paper production, e.g. paper waste, the production of paper e.g. retention aids, and the settlement of various organic or inorganic suspensions, i.e. refinery waste, food waste, etc. Likewise, enzyme broths and suspended mineral solids may be treated similarly. The dose of polymer effective for a particular application is generally found by routine experimentation in a manner well-known to those skilled in the art. Preferred doses range from about 0.1 parts of polymer per million (ppm) to about 10,000 ppm, based on the weight of the solids suspended in the substrate to be treated.

When the particles are produced in such a way that they are not water-soluble but are instead water-swellable, they may be dispersed in water to form aqueous mixtures comprised of dispersions of water-swellable polymers. Water-swellable polymers may be useful for applications such as thickening paint, in papermaking e.g. as described in U.S. Patent No. 5,274,055 and U.S. Patent No. 5,167,766, and as printing ink thickeners.

The following examples are set forth for illustration purposes only and are not to be construed as limits on the present invention.

Test Procedures

Standard viscosity is the viscosity of a 0.096% solution of water-soluble polymer in 1 N sodium chloride at 25°C, at a pH of 8.0 for nonionic and anionic polymers and at a pH of 7.0 for cationic polymers, except where noted. The viscosity was measured by a Brookfield LVT viscometer with a UL adapter at 60 rpm. The polymer solution being measured was made by preparing a 0.20% solution of polymer in deionized water during two hours and then diluting with the appropriate amounts of deionized water and sodium chloride.

Volatiles content (% loss on drying; LOD) was determined using a Sartorius Model MA30 Moisture Analyzer. The dry polymer sample was dried at a specified temperature either to a constant weight or for a specified time. A period of 30 minutes at 105°C provided a reliable and reproducible indicator of product volatiles content. The results are reported as weight percent volatiles based on the total weight.

Water analysis of the volatiles was performed by Karl Fisher titration. Residual oil levels in the dry products were determined by sample extraction with supercritical carbon dioxide and gas chromatography analysis of the extractant. Residual formaldehyde in the recovered oil was determined by stirring the recovered oil with water for thirty

minutes, then analyzing the water extractant by ion chromatography.

The laboratory spray dryer used in the Examples below was obtained commercially. The chamber of the laboratory spray dryer was 760 millimeters (mm) in diameter with a 860 mm verticle side and a 65 degree conical bottom. Nominal gas flow through the dryer was about 180 cubic meters per hour. The emulsion or microemulsion feed was fed at the center of the top of the chamber using a variable speed pump, through a two-fluid nozzle using air for atomization. The outlet gas temperature was controlled by varying the inlet gas temperature and feed rate. To provide an inert atmosphere, the dryer was supplied with nitrogen gas from a cryrogenic storage tank. The dried polymer product was discharged through the bottom of the dryer cone to a cycione where the dry product was removed and collected. Residence time in the dryer was generally about 10-15 seconds.

Some spray-drying Examples were performed with a commercial-scale 8.3 foot diameter closed cycle spray dryer equipped with a direct contact spray condenser.

Spray-dried polymer particle products were agglomerated using a commercial mechanical agglomerator in conjunction with a 10.76 square foot fluid bed dryer. The agglomerator had a vertical shaft and a flexible polymer housing, with a single shaft rotor having 2 or 3 pin or paddle-type mixing elements that rotated at 1500 to 5200 revolutions per minute (rpm). It was equipped with mechanically driven rollers that moved along the flexible polymer housing to prevent accumulation of material along the walls. The spray-dried product and binder e.g. water were fed to the top of the agglomerator; the spray-dried polymer by screw feeder, and the via spray nozzles. The agglomerates formed by agglomerating the spray-dried polymer particles dropped out of the bottom of the agglomerator and directly into a fluid bed-dryer, where the agglomerates were dried to the desired water content. Typical residence time in the agglomerator was about two seconds.

The purpose of the funnel flow test is to identify the funnel at which polymer particles and agglomerates fail to flow, both uncompacted and compacted. The funnel flow test is conducted using 5 funnels, numbered 1-5, respectively, having the following outlet diameters: 14 mm, 12 mm, 8 mm, 5 mm, 3.5 mm. The procedure is followed by starting with funnel 5 (oulet 3.5 mm), blocking the outlet, filling the funnel with the polymer to be tested, and unblocking the outlet to allow the polymer to flow. If all of the polymer passed \through the funnel, the polymer was given a score of +5. If the polymer failed to flow from the funnel when the outlet was unblocked, the procedure was repeated with funnel 4, funnel 3, etc. until flow was observed. The funnel number was

recorded when flow was not observed. The process was then repeated to determine the flow of compacted polymer, by tapping the funnel about twenty times (or placed on a suitable vibrating plate) to create compaction. For example, a polymer with a score of +5, +5 flowed through the No. 5 funnel on both tests, whereas a polymer with a score of +5, 3 flowed through the No. 5 funnel uncompacted, but would not flow through the No. 3 funnel when compacted.

The bulk density of polymer particles and agglomerates was determined by adding the particles or agglomerates to a suitable preweighed measuring container and "tapping" or slightly agitating the container to cause the particles or agglomerates to settle. The volume of the polymer was then read from the measuring container, the measuring container weighed, and the bulk density calculated in units of grams per cubic centimeter (g/cc).

Dissolving times were determined by adding a 0.2 parts of polymer particles or agglomerates to 99.8 parts of deionized water in a suitable vessel and stirring with a magnetic stir bar. The bulk viscosity of the mixture was measured at regular intervals e.g. five or ten minutes, using a Brookfield LVT viscometer with a UL adapter at 60 rpm, until a maximum bulk viscosity was reached, e.g. until no further increase in bulk viscosity was observed. The time to achieve this maximum bulk viscosity was recorded as the dissolving time and was generally no more than a few hours.

In the following Examples, the quaternized Mannich polyacrylamide microemulsions (Cat-PAM) were prepared as in U.S. Patent No. 4,956,399, except that Isopar G was used as the oil. The hydrolyzed polyacrylamide emulsions were prepared as described in U.S. Patent No. 5,286,806, except that Isopar G was used as the oil. Highly crosslinked acrylamide/acrylic acid emulsion and microemulsion copolymer microbeads were prepared as described in U.S. Patent No. 5,274,055, except that Isopar G was used as the oil. Cationic emulsion copolymers of (meth)acryloxyethyltrimethylammonium chloride and acrylamide, and anionic copolymers of acrylic acid and acrylamide, were prepared by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393, and branched cationic polymers were prepared as in U.S. Patent No. 6,147,176, except that Isopar G was used as the oil in all cases. In all cases, the substitution of Isopar G for the other oil was on a volume basis.

Polymer particle and agglomerate sizes were determined by commercially available light scattering instrumentation and by conventional sieve techniques.

EXAMPLE 1

A quaternized Mannich polyacrylamide microemulsion (Cat.PAM) having a Standard Viscosity of about 2.5 was spray dried in a laboratory spray dryer using a two-fluid nozzle in a nitrogen atmosphere with gas inlet and outlet temperatures of 182°C and 92°C respectively. The volatiles were 7.65% and the residence time was 14 seconds. The Standard Viscosity of a solution of the dry product was 2.25 cps, 9.3% less than the standard viscosity of a solution of the microemulsion product. The polymer particles ranged in size from about 19 to about 900 microns. The level of residuals in the dry product were as follows: formaldehyde: 520 ppm; methyl chloride: less than 100 ppm; dimethylamine hydrochloride: 3724 ppm; trimethylamine hydrochloride: 6248 ppm; tetramethylammonium hydrochloride: 5219 ppm.

EXAMPLE 2 (Comparative)

The Cat.PAM of Example 1 was dried on a 12-inch by 18-inch vacuum double drum dryer with less satisfactory results. The steam temperature on the drum was 115°C. and the steam pressure on the drums was 10 psig. The drum was operated at 6 revolutions per minute with a drum clearance of 0.010 inches and with a vacuum of about 65 mm Hg. The feed rate was about 90 pounds of emulsion per hour. The percent volatiles and Standard Viscosity are set forth in Table 1. A comparison of the dry polymer produced herein to that of Example 1 shows that the Standard Viscosity was significantly reduced using the drum dryer.

Table 1

Ex. No.	Emulsion Name	Gas Inlet/Outlet Temperature °C	Residence Time, sec.	Volatiles (LOD), %	Polymer Emulsion Standard Viscosity, cps	Dry Product Standard Viscosity, cps.	Change in Standard Viscosity %
1	Cat.PAM	182/92	14	7.65	2.48	2.25	-9.3
2C	Cat.PAM (drum dried)	N/A	N/A	9.9	2.48	1.98	-20.2

C: Comparative Example

EXAMPLES 3-7

A Cat.PAM having a Standard Viscosity of about 2.5 was spray dried using an 8.3 foot diameter commercial spray dryer with a rotary (spinning disk) atomizer. The dryer was operated using air on a once-through basis. The various temperatures and residence time conditions used are described in Table 2; residence time was 30 seconds for all of the runs. Product was collected both at the base of the dryer (chamber) and at the discharge of a cyclone located immediately after the dryer. Table 2 also shows the analytical results of Examples 3-7; in each case, polymer product from each of the two collection points (chamber and cyclone) was analyzed with the results as shown. In each case, the Standard Viscosity of the polymer particles was within 15% of the Standard Viscosity of the corresponding Cat.PAM.

Table 2

Ex. No.	Emulsion Name	Gas Inlet/ Outlet Temp. °C	Atomizer Speed, rpm	Collection Point	Volatile (LOD), %	Polymer Emulsion Standard Viscosity, cps	Dry Product Standard Viscosity cps	Change in Standard Viscosity %
3	Cat.PAM	138/86	19,500	chamber	8.59	2.44	2.45	+ 0.4
				cyclone	9.64	2.44	2.60	+ 6.6
4	Cat.PAM	178/93	17,100	chamber	8.91	2.44	2.44	0
				cyclone	9.71	2.44	2.59	+ 6.2
5	Cat.PAM	181/92	15,800	chamber	8.40	2.44	2.40	- 1.6
				cyclone	9.42	2.44	2.58	+ 5.7
6	Cat.PAM	173/81	15,800	chamber	9.14	2.44	2.40	- 1.6
				cyclone	10.93	2.44	2.58	+ 5.7
7	Cat.PAM	171/81	13,400	chamber	10.34	2.44	2.38	- 2.5
				cyclone	10.85	2.44	2.49	+ 2.1

EXAMPLES 8-12

A Cat.PAM having a Standard Viscosity of about 2.5 was spray dried using an 8.3 foot diameter commercial spray dryer with a pressure nozzle atomizer. The dryer was operated as a closed cycle system using nitrogen gas. Product was collected at the base of the dryer or chamber. After recovering the polymer, the outlet gas was passed through a direct contact condenser and the resulting aqueous and Isopar G layers were separated. The cooled gas was then reheated and returned to the inlet of the dryer; a very small fraction was vented. The level of residual formaldehyde in the recovered Isopar G was 0.09 milligrams/kilogram, as measured after the completion of the five runs. The quality of the recovered Isopar G was such that it could be recycled and used directly for further microemulsion or emulsion polymerizations. Table 3 provides the various process conditions; the residence time for all runs was 24 seconds. The properties of the resulting dry polymer particles are also shown in Table 3. One to three samples of the polymer product were collected for each run and analyzed as

shown. In each case, the Standard Viscosity of the polymer particles was within 15% of the Standard Viscosity of the initial Cat.PAM used to spray dry.

Table 3

Ex. No.	Emulsion Name	Gas Inlet/ Outlet Temp. °C	Nozzle Orifice Size. mm	Sample #	Volatiles (LOD). %	Polymer Emulsion Standard Viscosity. cps	Dry Product Standard Viscosity. cps.	Change in Standard Viscosity %
8	Cat.PAM	177/86	1.4	1	9.70	2.49	2.36	- 5.2
				2	9.64	2.49	2.16	- 13.3
9	Cat.PAM	183/90	1.3	1	11.76	2.49	2.57	+ 3.2
				2	11.67	2.49	2.48	- 0.4
				3	10.28	2.49	2.46	-1.2
10	Cat.PAM	184/91	1.3	1	8.12	2.49	2.20	- 11.7
11	Cat.PAM	145/91	0.8	1	9.15	2.49	2.21	- 11.2
				2	9.57	2.49	2.42	- 2.8
12	Cat.PAM	164/93	1.04	1	6.80	2.49	2.32	- 6.8
				2	8.53	2.49	2.30	- 7.6

EXAMPLE 13

A Cat.PAM having a Standard Viscosity of about 2.5 was buffered with urea/lactic acid to pH 4.5, then heat treated by heating to 67-70°C for 7-9 hours, then allowed to cool to ambient temperature. This heat treatment process is described in U.S. Patent No. 5,627,260. The resulting polymer microemulsion was then spray dried in a laboratory spray dryer using a two-fluid nozzle. The various temperatures and residence time conditions used are described in Table 4. As shown in the Table, the Standard Viscosity of the polymer particles was within 15% of the Standard Viscosity of the corresponding heat treated Cat.PAM. The levels of residuals in the dry product were as follows: formaldehyde: 510 ppm; methyl

chloride: less than 100 ppm; dimethylamine hydrochloride: 7500 ppm; trimethylamine hydrochloride: 6928 ppm; tetramethylammonium hydrochloride: 4671 ppm.

Table 4

No.	Emulsion Name	Gas Inlet/ Outlet Temp.°C	Volatiles (LOD), %	Residence Time, sec.	Polymer Emulsion Standard Viscosity, cps	Dry Product Standard Viscosity, cps	Change in Standard Viscosity, %
13	Cat.PAM (heat treated)	200/92	5.6	14	2.51	2.17	-13.5

EXAMPLE 14

Cat.PAM polymer particles were obtained by the spray drying process of Example 1. To 97.5 parts of these granules was added 2.5 parts of sodium carbonate in a suitable vessel. The vessel was mechanically shaken for 30 minutes to form a composition containing substantially dry granules of quaternized Mannich polyacrylamide and sodium carbonate.

EXAMPLE 15

Particles of Cat.PAM were obtained by the spray drying process of Example 13 and then sodium carbonate was added according to the process of Example 14. Solutions of the particles were prepared by dissolving 0.2 parts of the particles in 100 parts water. The dry particles took approximately 1 hour to dissolve. A sample of the heat treated polymer microemulsion described in Example 13 was also dissolved in water to produce a similar polymer concentration. Both polymers were allowed to stir in water for two hours, then were tested for their ability to flocculate suspended solids using a 2.0% solids digested sewage sludge. Approximately 200 parts of the sludge was mixed at about 1000 rpm with various amounts of the polymer solutions, ranging from 10 parts to 50 parts, for about 5 seconds. Thereafter, the drainage rates of the flocculated solids were measured at 10, 20 and 30 seconds. The polymer products both performed equally well in the dose range of 25 to 30 pounds of polymer per ton of sludge.

EXAMPLE 16

Particles of Cat.PAM were prepared according to Example 14, except that sodium bicarbonate was used in place of sodium carbonate. The Standard Viscosity of these particles was determined, without adjustment of the pH, to be 2.45 cps. In comparison, the Standard Viscosity (measured without pH adjustment) of particles of Cat.PAM prepared by the procedure of Example 1, which did not contain a base, was measured as 1.3 centipoise. Standard Viscosity is known in the art to directly correlate with polymer performance, e.g., flocculation.

EXAMPLE 17C

A polyacrylamide microemulsion was prepared as follows: To 143.75 parts of Isopar G, 26.28 parts Atlas G-1086 and 6.57 parts Arlacel* 83, were slowly added 172.93 parts of a pH 3.0 aqueous solution containing acrylamide (148.2 parts of 53.3% solution), sodium bromate (1.16 parts of 1% solution), 0.68 parts isopropanol, and ethylenediaminetetraaceteic acid (0.40 parts of 40% solution) with stirring. The resulting monomer microemulsion was sparged for 40 minutes with nitrogen. SO_2 gas was then bubbled into the resultant microemulsion and the polymerization temperature was kept below 65°C. The resulting product was a clear stable microemulsion having a standard viscosity of 3.07 centipoise.

EXAMPLE 18

The procedure of Example 17C was followed except that Isopar G recovered by following the process of Examples 8-12 was used in place of the fresh Isopar G. The resulting product was a clear stable microemulsion having a standard viscosity of 3.03 centipoise, virtually the same standard viscosity as was obtained using fresh Isopar G (Example 17C).

EXAMPLES 19-23

A 20% hydrolyzed polyacrylamide emulsion having a polymer solids of 23.8% and a Standard Viscosity of 8.63 centipoise was prepared as described in U.S. Patent

*Trade-mark

No. 5,286,806, except that Isopar G was used as the oil, then spray dried in a laboratory spray dryer using nitrogen. The inlet temperature, outlet temperature and feed rate were varied, and the LOD, Standard Viscosity (SV), and drying loss of the polymer particle product were measured as shown in Table 5. Smaller drying losses were observed at outlet temperatures of less than 100° C.

Table 5

No.	Inlet Temp., °C	Outlet Temp.,°C	Feed Rate, ml/min.	LOD, %	Product SV, cp	Drying Loss, %
19	162	82	96	10.2	8.43	2.3
20	161	84	64	7.8	8.31	3.7
21	193	96	52	5.6	8.21	4.9
22C	227	115	44	3.6	8.11	6.0
23C	253	132	36	2.2	7.48	13.3

C: Comparative Example

EXAMPLES 24-36

A series of 13 water-soluble or water-swellable vinyl-addition polymer containing water-in-oil emulsions and water-in-oil microemulsions were prepared according to the methods referenced below (except that Isopar G was used as the oil), then spray dried in a laboratory spray dryer using nitrogen, and the results obtained in Table 6 were obtained. Hydrolyzed PAM emulsions were obtained by hydrolyzing polyacrylamide (PAM) emulsions as described in U.S. Patent No. 5,286,806 (Example 24-25). Acrylamide (AMD) and acrylic acid (AA) were emulsion copolymerized to yield AMD/AA emulsions by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393 (Examples 26-27). A hydroxamated acrylamide polymer with a degree of hydroxamation of about 40% (40% HX emulsion Example 28) was prepared by the methods of U.S. Patent No. 4,767,540. The acrylamide/acrylic acid microbead microemulsion of Example 29 was prepared by the methods of U.S. Patent No. 5,274,055. The water-soluble polyacrylate ester emulsion was prepared by the method of U.S. Patent No. 5,847,056 (Example 30). Acrylamide and acryloxyethyltrimethylammonium chloride (AETAC) were emulsion copolymerized to yield AMD/AETAC emulsions by known

methods e.g. Vanderhoff, U.S. Patent No. 3,284,393 (Examples 31-34); small amounts e.g. about 4 molar parts per million, based on monomers, of methylenebisacrylamide were added to the AMD/AETAC polymers of Examples 32 and 34 to create branching, see e.g. U.S. Patent No. 6,147,176. Mannich and quaternized Mannich microemulsions were prepared by the methods of U.S. Patent No. 4,956,399 (Examples 35 and 36). In each case, substantially dry, free flowing mixtures of polymer particles having drying losses of about 15% or less were obtained.

Table 6

Ex. No.	Type	Solids	Standard Viscosity (cP)	Feed Rate, ml/min	Inlet Temp., °C	Outlet Temp., °C	Dry Product LOD, %	Dry Product SV, cP	Drying Loss, %
24	10% hydrolyzed PAM emulsion	24.5	7.51	60	164	85	5.6	7.34	2.2
25	40% hydrolyzed PAM emulsion	22.2	10.63	52	165	84	6.5	10.39	2.3
26	70/30 AMD/AA emulsion	34.9	7.94	80	165	86	9.0	8.22	0.6
27	20/80 AMD/AA emulsion	34.7	9.30	96	162	87	6.0	8.82	5.2
28	40% HX emulsion	10.6	12.6	45	174	88	6.1	11.4	9.5
29	40/60 AMD/AA microbead micro-emulsion	28.0	1.34	40	189	92	5.0	1.40	4.5
30	Polyacrylate ester emulsion	19.3	7.9	60	166	85	6.7	7.43	5.9

31	90/10 AMD/ AETAC emulsion	37.1	4.07	80	159	85	5.1	3.81	6.4
32	60/40 AMD/ AETAC branched emulsion	37.8	1.77	95	171	88	4.9	1.77	0
33	45/55 AMD/ AETAC emulsion	47.0	3.60	160	169	81	10.4	3.65	1.4
34	45/55 AMD/ AETAC branched emulsion	45.3	3.39	96	161	88	5.7	3.39	0
35	Mannich microemulsion	23.6	3.42	88	152	82	10.8	3.39	0.9
36	Quaternized Mannich microemulsion	29.8	2.6	160	161	84	6.8	2.46	5.4

EXAMPLE 37-39

A 20% hydrolyzed polyacrylamide emulsion made with isopar G was spray-dried on a commercial scale 8.3 foot diameter spray dryer using a direct contact spray condenser. Spray-dry process-generated water and oil were collected and acidified, the layers separated, and the upper Isopar G layer recovered. Side-by-side laboratory-scale acrylamide polymerizations were then performed using the recovered Isopar G and virgin Isopar G. The Standard Viscosity of the polyacrylamide made using the recovered oil was 6.58 cps, virtually the same as the Standard Viscosity of the polyacrylamide made using the virgin oil, 6.67 cps. Subsequently, an acrylamide polymerization was carried out on a 200-gallon scale using the same recovered Isopar G and the same recipe as the laboratory scale batch. The resultant polyacrylamide had a Standard Viscosity of 6.55 cP, essentially the same as the laboratory batch.

EXAMPLES 40-41

A quaternized Mannich polyacrylamide microemulsion having a Standard Viscosity of about 2.1 was spray dried as in Example 1. Both the microemulsion and the polymer particles were placed into an oven at 90°C, and the Standard Viscosities determined at various times, as shown in Table 7. The decrease in the Standard Viscosity of the microemulsion sample was much greater than the modest decrease observed for the spray-dried polymer, in spite of the relatively severe conditions.

Table 7

Time (minutes)	Example 40 Standard Viscosity of Spray-Dried Polymer	Example 41 C (Comparative) Standard Viscosity of Microemulsion Polymer
0	1.86	2.1
15	1.66	1.25
30	1.52	1.15
60	1.47	1.10

EXAMPLES 42-43

A quaternized Mannich polyacrylamide microemulsion having a Standard Viscosity of about 2.5 was spray dried as in Example 1. Both the microemulsion and the polymer particles were stored at room temperature, and the Standard Viscosities determined at various times, as shown in Table 8. The Standard Viscosity of the spray-dried polymer was essentially unaffected by the passage of time, whereas the Standard Viscosity of the microemulsion polymer decreased noticeably.

Table 8

Time (days)	Example 42 Standard Viscosity of Spray-Dried Polymer	Example 43 C (Comparative) Standard Viscosity of Microemulsion Polymer
5	2.25	
14	2.44	
19		2.48
24	2.36	
45		2.11
46	2.44	
58		2.09
63	2.36	
75		1.90
98	2.38	
103		1.84
215	2.37	
257		1.70

EXAMPLES 44-49

An 20% anionic hydrolyzed PAM emulsion was obtained by hydrolyzing a polyacrylamide (PAM) emulsion as described in U.S. Patent No. 5,286,806. A 55% cationic emulsion was obtained by copolymerizing acrylamide and acryloxyethyltrimethylammonium chloride (AETAC) by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393. A Cat.PAM was was obtained as in U.S. Patent No. 4,956,399. In each case, Isopar G was used as the oil. Part of each sample was precipitated in hexane/acetone, then dried under vacuum to produce a polymer powder. Part of each sample was also spray-dried, and part of each spray-dried sample was agglomerated. Bulk density, flow properties (funnel flow test), dissolving time and

particle size were determined and are shown in Table 9. Particle size was determined by light scattering for the precipitated and spray-dried polymers, and by sieve screening for the agglomerates.

Table 9

Ex. No.	Polymer	Bulk Density, g/cc	Funnel Flow	Dissolving Time, min.	Particle Size Distribution
44C	20% Anionic Precipitated	0.26	1,1	90	90% < 109 microns 50% < 42 microns 10% < 8 microns
45	20% Anionic Spray-dried	0.79	1,1	85	90% < 148 microns 50% < 65 microns 10% < 27 microns
46	20% Anionic Spray-dried and Agglomerated	0.53	4,3	20-25	90% < 850 microns 50% < 350 microns 10% < 170 microns
47C	55% Cationic Precipitated	0.30	1,1	80	90% < 18 microns 50% < 11 microns 10% < 5 microns
48	55% Cationic Spray-dried	0.86	1,1	60-65	90% < 156 microns 50% < 68 microns 10% < 22 microns
49	55% Cationic Spray-dried and Agglomerated	0.52	4,3	25-30	90% < 1500 microns 50% < 600 microns 10% < 260 microns
50C	Cat.PAM Precipitated	0.164	1,1	80	90% < 58 microns 50% < 27 microns 10% < 17 microns
51	Cat.PAM Spray-dried	0.86	1,1	60-65	90% < 152 microns 50% < 72 microns 10% < 20 microns
52	Cat.PAM Spray-dried and Agglomerated	0.52	4,3	25-30	90% < 1600 microns 50% < 560 microns 10% < 280 microns

C: Comparative Example

EXAMPLES 53-55

The agglomerates of Examples 46, 49 and 52 were screened to remove agglomerates larger than about 1190 microns and smaller than about 177 microns. The resultant screened agglomerates had improved flow properties and dissolving times relative to the agglomerates of Examples 46, 49 and 52 as shown in Table 10.

Table 10

Example No.	Screened Agglomerate	Bulk Density, g/cc	Funnel Flow	Dissolving Time, min.
53	20% Anionic	0.5	5,4	20
54	55% Cationic	0.51	5,4	20-25
55	Cat.PAM	0.51	5,4	< 15

EXAMPLES 56-63

Anionic hydrolyzed PAM emulsions were obtained by hydrolyzing polyacrylamide (PAM) emulsions as described in U.S. Patent No. 5,286,806, an 80% anionic emulsion was obtained by copolymerizing acrylamide and acrylic acid (AMD/AA) by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393, and a Mannich microemulsion was obtained as described in U.S. Patent No. 4,956,399, except that Isopar G was used as the oil in all cases. Each emulsion and microemulsion was spray-dried according to the conditions shown in Table 11. Smaller drying losses and faster dissolving times were observed when spray-drying was conducted at lower outlet temperatures.

75365-152

Table 11

Example No.	Polymer	Inlet/Outlet Temperature, °C	Drying Loss, %
56	20% Hydrolyzed Anionic PAM emulsion	162/82	4.6
57	20% Hydrolyzed Anionic PAM emulsion	253/132	15.4
58	40% Hydrolyzed Anionic PAM emulsion	162/84	4.0
59	40% Hydrolyzed Anionic PAM emulsion	265/127	18.8
60	20/80 AMD/AA emulsion	163/86	4.8
61	20/80 AMD/AA emulsion	225/120	14.5
62	Mannich microemulsion	155/83	6.8
63	Mannich microemulsion	265/130	62.5

EXAMPLES 64-65

A blend of a Cat.PAM and a cationic copolymer is prepared as in U.S. Patent No. 5,914,366, and a cationic polymer dispersion is prepared according to the procedures of U.S. Patent No. 4,506,062 (without distillation), except that Isopar G is used as the oil. The blend and the dipersion are spray-dried in a laboratory spray-dryer as in Examples 24-36. Substantially dry polymer particles are obtained, with drying losses of about 15% or less. Greater than 90% of the spray-dried blend particles contain both the Cat.PAM and the cationic copolymer.

CLAIMS:

1. Polymer agglomerates comprised of porous polymer particles having at least one opening in their walls, wherein said agglomerates have a size in the range of about 120 to about 1500 microns, wherein at least about 5% of said agglomerates are larger than about 900 microns, and wherein said agglomerates are comprised of a water-scluble vinyl-addition polymer, or a crosslinked water-insoluble vinyl-addition polymer which would be water-soluble if not crosslinked, (i) having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt, or (ii) containing recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate.

2. Polymer agglomerates as claimed in claim 1, wherein said agglomerates are comprised of a water-soluble vinyl-addition polymer and are substantially free of water-insoluble vinyl-addition polymer.

3. Polymer agglomerates as claimed in claim 1, wherein said vinyl-addition polymer has pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt.

4. Polymer agglomerates as claimed in claim 1, wherein said vinyl-addition polymer contains recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate.

5. Polymer agglomerates as claimed in claim 1, 2, 3 or 4, wherein at least about 10% of said agglomerates are larger than about 900 microns.

6. Polymer agglomerates as claimed in claim 1, 2, 3, 4 or 5, wherein said agglomerates are comprised of two or more different vinyl-addition polymers.

7. A method of treating suspended solids, comprising (a) intermixing the polymer agglomerates of any one of claims 1 to 6 with water to form an aqueous mixture, (b) intermixing said aqueous mixture with suspended solids, and (c) separating resultant concentrated solids from resultant aqueous liquid.

8. A method as claimed in claim 7, wherein said suspended solids comprise mineral solids, paper waste, cellulosic solids, or a biologically treated suspension.

9. A polymer composition comprised of (a) porous polymer particles having at least one opening in their walls and (b) polymer particles that do not have at least one opening in their walls, wherein said (a) and (b) are comprised of a water-soluble, acetone-insoluble, vinyl-addition polymer, or a crosslinked water-insoluble vinyl-addition polymer which would be water-soluble and acetone-insoluble if not crosslinked, (i) having pendant groups

selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt, or (ii) containing recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate, and wherein said (a) and (b) have a size in the range of about 200 microns to about 1200 microns.

10. A polymer composition as claimed in claim 9, wherein said (a) and (b) are comprised of a water-soluble vinyl-addition polymer and are substantially free of water-insoluble vinyl-addition polymer.

11. A polymer composition as claimed in claim 9 or 10, wherein said polymer composition is obtained by spray-drying a vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion.

12. A polymer composition as claimed in clain 11, wherein said polymer composition dissolves in water at a rate that is faster than the dissolution rate for a polymer powder obtained by precipitating said polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion in hexane/acetone and vacuum drying.

13. A polymer composition as claimed in claim 9, 10, 11 or 12, wherein said vinyl-addition polymer has pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, and hydroxamic acid salt.

14. A polymer composition as claimed in claim 9, 10, 11 or 12, wherein said vinyl-addition polymer contains recurring units selected from the group consisting of dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate.

15. A polymer composition as claimed in claim 9, 10, 11, 12, 13 or 14, wherein said (a) and (b) are comprised of two or more different vinyl-addition polymers.

16. A method of treating suspended solids, comprising (a) intermixing the polymer composition of any one of claims 9 to 15 with water to form an aqueous mixture, (b) intermixing said aqueous mixture with suspended solids, and (c) separating resultant concentrated solids from resultant aqueous liquid.

17. A method as claimed in claim 16, wherein said suspended solids comprise mineral solids, paper waste, cellulosic solids, or a biologically treated suspension.

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(54) COMPOSITION PULVERULENTE
(54) POWDER COMPOSITION

(57)

A powder composition characterized in that it comprises defatted yolk particles and a functional food material and that the functional food material has been infiltrated into pores present in the defatted yolk particles; a process for producing a powder composition characterized by mixing defatted yolk with water, spray-drying the resultant mixture to prepare defatted yolk particles which are porous and have pores on the surfaces, mixing the resultant defatted yolk particles with a functional food material, and vacuum-drying the resultant mixture; and a food comprising the powder composition. The powder composition is highly flowable and tack-free, can contain the functional food material in a high concentration, prevents the deterioration of a substance susceptible to deterioration by light, heat, oxygen, etc., improves the undesirable flavor of a substance, and stably retains the components of the functional food material over long.

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A powder composition characterized in that it comprises defatted yolk particles and a functional food material and that the functional food material has been infiltrated into pores present in the defatted yolk particles; a process for producing a powder composition characterized by mixing defatted yolk with water, spray-drying the resultant mixture to prepare defatted yolk particles which are porous and have pores on the surfaces, mixing the resultant defatted yolk particles with a functional fooc material, and vacuum-drying the resultant mixture; and a food comprising the powder composition. The powder composition is highly flowable and tack-free, can contain the functional food material in a high concentration, prevents the deterioration of a substance susceptible to deterioration by light, heat, oxygen, etc., improves the undesirable flavor of a substance, and stably retains the components of the functional food material over long.

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(57) Abstract

A powder composition characterized in that it comprises defatted yolk particles and a functional food material and that the functional food material has been infiltrated into pores present in the defatted yolk particles; a process for producing a powder composition characterized by mixing defatted yolk with water, spray-drying the resultant mixture to prepare defatted yolk particles which are porous and have pores on the surfaces, mixing the resultant defatted yolk particles with a functional food material, and vacuum-drying the resultant mixture; and a food comprising the powder composition. The powder composition is highly flowable and tack-free, can contain the functional food material in a high concentration, prevents the deterioration of a substance susceptible to deterioration by light, heat, oxygen, etc., improves the undesirable flavor of a substance, and stably retains the components of the functional food material over long.

DESCRIPTION

POWDER COMPOSITION

TECHNICAL FIELD

The present invention relates to a powder composition. More specifically, it relates to a powder composition suitably used for foods, cosmetics, pharmaceuticals, and the like.

BACKGROUND ART

Since many of the biologically active substances used for foods, cosmetics, pharmaceuticals, and the like have poor flavor and undesired tastes, odors, and the like, it has been difficult to have intake of biologically active substances in an amount sufficient for exhibiting their effects. In addition, many of the biologically active substances have a property of being susceptible to undergo denaturation and lose activity, and decomposition by heat, light, oxidation, or the like. Therefore, when these biologically active substances are tried to be used for foods, food materials, and the like in a dry state, there arises a problem that their activity is easily lost during the process of general process treatments such as drying, powdering, and the like.

For instance, in a fat-soluble provitamin β-carotene, there arise such problems that fading in the drying and powdering process takes place, and that nearly a half of its biological activity is lost. As a method for obtaining a stable β-carotene powder, there has been proposed a method comprising preparing inclusion compounds with cyclodextrin around liquid or pasty β-carotene, whereby increasing the stability of the β-carotene during powdering (Japanese Patent Laid-Open Nos. Sho 62-267261 and Hei 4-281754).

However, even when the above methods were employed, an effect of preventing oxidation degradation of the β-carotene by light or heat is insufficient, so that only the powder in which the β-carotene content is lowered can be obtained.

As described above, the substances susceptible to undergo oxidation degradation require careful attention in the process such as production, storage, manufacturing of preparation, requiring a complicated process, so that its application is largely limited.

In addition, since the tea extract generally is bitter while having various excellent functional properties, it has been difficult to take the tea extract at high concentrations.

Therefore, the present inventors have developed a

functional protein preparation obtained by adding an organic solvent such as ethanol to egg yolk powder, delipidating the egg yolk, thereafter mixing the delipidated product obtained by drying *in vacuo* with a biologically active substance, and subsequently drying (Japanese Patent Laid-Open No. Hei 9-9878).

Although the functional protein preparation mentioned above surely has anti-oxidation ability and flavors of acceptable levels, since the biologically active substance is deposited on the surfaces of the delipidated product, the preparation is sticky, and operability such as measuring, mixing, filling, and the like of the resulting preparation cannot be said to be favorable. Therefore, the development of the functional protein preparation with improvement in the stickiness mentioned above is desired.

DISCLOSURE OF INVENTION

An object of the present invention is made in view of the prior art described above, and is to provide a powder composition which has excellent flowability owing to its lowered stickiness and can contain a functional food material at high concentrations, thereby preventing the deterioration of the substances susceptible to undergo deterioration by light, heat, oxygen, or the like, in which the flavor of the substance having an undesired

flavor is improved, whereby giving a powder composition in which the properties of the functional food material are stable for a long period of time.

According to the present invention, there can be provided:

[1] a powder composition, characterized in that the powder composition comprises delipidated egg yolk particles and a functional food material, the functional food material being impregnated in pores of the delipidated egg yolk particles;

[2] a method for preparing a powder composition characterized by mixing a delipidated egg yolk with water, spray-drying the resulting mixture, to prepare porous, delipidated egg yolk particles having pores on surfaces thereof; and mixing the resulting delipidated egg yolk particles with a functional food material, and drying the resulting mixture under reduced pressure; and

[3] a food comprising the powder composition mentioned above.

BEST MODE FOR CARRYING OUT THE INVENTION

The powder composition of the present invention comprises delipidated egg yolk particles and a functional food material, the functional food material being impregnated in pores of the delipidated egg yolk

particles.

The delipidated egg yolk used during the process of producing the delipidated egg yolk particles can be obtained by removing lipids from an egg yolk by a known method.

The egg yolk mentioned above is not particularly limited as long as it is one usually acceptable from the aspect of food hygiene. Examples of the egg yolk include raw egg yolk, egg yolk powder, sugared egg yolk, salted egg yolk, and the like. Among these egg yolks, the egg yolk powder obtained by drying by such a means as spray-drying can be favorably used in the present invention, from the viewpoint of easiness in handleability of the raw materials.

The method for removing the lipids from an egg yolk mentioned above is not particularly limited as long as it is a method usually employed in the manufacturing of foods. Examples of such methods include solvent extraction method, enzyme decomposition method, pressure extraction method, centrifugation method, supercritical extraction method, isolation method with an absorbent, and the like. Among these methods, the solvent extraction method is a method favorably employed in the present invention from the viewpoint of simplicity.

The solvent extraction method includes a method, for

instance, comprising sufficiently stirring an egg yolk and a solvent with a stirring device such as a homomixer, and subjecting the mixture to solid-liquid isolation by filtration, centrifugation, or the like.

The solvent mentioned above is not particularly limited as long as it is one usually acceptable as food hygiene. Examples of the solvent include ethanol, acetone, hexane, and the like. Among these solvents, ethanol is favorably used in the present invention from the viewpoint of safety. The amount of the above solvent is not particularly limited, and it is desired that the amount is from 400 to 5,000 parts by weight or so, preferably from 1,000 to 3,000 parts by weight or so, based on 100 parts by weight of the raw material egg yolk on a solid basis, from the viewpoints of the delipidation efficiency from the egg yolk and the economic advantages.

The temperature during stirring the egg yolk mentioned above with the solvent is not particularly limited, as long as it is a temperature at which the solvent mentioned above is in a liquid state. It is desired that the temperature is usually from 10° to 80°C or so, from the viewpoints of delipidation efficiency and safety when handling a solvent. In addition, the stirring time cannot be absolutely determined because it differs in accordance with the amounts of the egg yolk and the

solvent, the ability of the stirring device, and the like. It is usually desired that the stirring is carried out until the egg yolk is sufficiently dispersed in the solvent.

The delipidated egg yolk can be obtained by stirring the egg yolk and the solvent in the manner described above, and thereafter subjecting the mixture to solid-liquid isolation by filtration, centrifugation, or the like.

The lipid content of the delipidated egg yolk is not particularly limited. It is desired that the lipid content is 10% by weight or less, preferably 5% by weight or less, of the solid ingredients of the delipidated egg yolk. The method for measuring the lipid content of the delipidated egg yolk is not particularly limited. Examples of such a method include usual method for measuring lipid content for foods such as methanol-chloroform liquid mixture method.

The properties of the delipidated egg yolk may be either powder or liquid.

In addition, the delipidated egg yolk may contain a solvent which can be used for food processing. The content of the above solvent is not particularly limited.

The delipidated egg yolk particles (particles constituting the delipidated egg yolk powder, usually

referred to as "delipidated egg yolk particles") used in the present invention is prepared from the delipidated egg yolk. The method for preparing the delipidated egg yolk particles mentioned above includes a method, for instance, comprising mixing the delipidated egg yolk with water, spray-drying the resulting mixture, to prepare delipidated egg yolk particles having pores on the surfaces thereof. One of the largest features of the present invention resides in that there is employed an operation of mixing the delipidated egg yolk with water, and spray-drying the resulting mixture. Since such an operation is employed in the present invention, the resulting delipidated egg yolk particles are porous, on which surfaces there can be surprisingly formed a large number of pores (pore size being from about 0.1 to 10 μm) which cannot be found in the conventional delipidated egg yolk particles. In Japanese Patent Laid-Open No. Hei 9-9878, there is employed drying *in vacuo*. In this method, however, pores are not formed.

Water used during the manufacturing of the egg yolk particles mentioned above include, for instance, deionized water, tap water, distilled water, electrolytic water, and the like, and the present invention is not limited to those exemplified above.

It is desired that the mixing proportion of the

delipidated egg yolk to water, based on 100 parts by weight of the delipidated egg yolk is such that the amount of water is usually 10 parts by weight or more, preferably 50 parts by weight or more, from the viewpoints of homogeneously dissolving and dispersing the delipidated egg yolk, and adjusting the balance of the hydrophilic groups and the hydrophobic groups on the surface of the delipidated egg yolk, and that the amount of water is 1,000 parts by weight or less, preferably 500 parts by weight or less, from the viewpoint of the efficiency during drying.

It is preferable that the mixing of the delipidated egg yolk with water mentioned above is usually carried out until which both ingredients are homogeneously dispersed. The resulting mixture thus obtained from the delipidated egg yolk and water is subsequently spray-dried.

The method for spray-drying mentioned above includes, for instance, a method for spraying from a high-pressure nozzle, and a method for spray-drying utilizing a centrifugal force, such as an atomizer. Incidentally, the hot air temperature during spray-drying is not particularly limited, as long as it is a dryable temperature. It is desired that the hot air temperature is usually from 50° to 200°C, preferably from 100° to 180°C. As a pressure when spray-drying using a

high-pressure nozzle, a pressure from normal pressure to 240 kg/cm^2 can be employed. In the spray-drying employing a high-pressure nozzle, it is desired that the pressure is usually from 20 to 100 kg/cm^2. Incidentally, it is preferable that the above spray-drying is carried out until which the water content of the resulting delipidated egg yolk particles becomes 10% or less.

The delipidated egg yolk particles obtained in the manner described above are porous and have pores on the surfaces thereof as described above.

Subsequently, the resulting delipidated egg yolk particles are mixed with the functional food material.

The functional food material used in the present invention is not particularly limited. Examples of the functional food material include substances having an undesirable flavor, substances susceptible to undergo deterioration, and the like.

The substances having an undesirable flavor mentioned above are not particularly limited. Examples of the above substances having an undesirable flavor include flavors pertaining to such tastes as bitter taste, puckery taste, hot taste, sour taste, and pungent taste, and in some cases sweet taste, tastiness (umami), and the like are also undesirable tastes. Examples thereof include substances having a flavor pertaining to odors such as

fish odor, plant odor, fermented odor, rotten odor, animal odor, acidification odor, burning odor, sweet odor, and sour odor. These substances having an undesirable flavor may be natural ones or synthesized ones as long as they can be used for foods. In addition, each of the substances having an undesirable flavor may be used alone, or in admixture of two or more kinds.

The substances having a bitter taste or puckery taste mentioned above are not particularly limited. Examples of the above substances having a bitter taste or puckery taste include extracts derived from plants. Concrete examples of the extracts derived from plants mentioned above include tea extracts, algae extracts, soybean extracts, quillate extracts, coffee bean extracts, and the like. Ingredients contained in these substances having a puckery taste include polyphenol compounds, isoflavone compounds, carotenoid compounds, saponin, caffeine, amino acids, inorganic salts, and the like. The inorganic salts mentioned above are not particularly limited. Examples of the above inorganic salt include iron salts, calcium salts, magnesium salts, zinc salts, sodium salts, potassium salts, phosphorates, and the like. These substances having a bitter taste or puckery taste can be used alone or in admixture of two or more kinds.

The substances having a hot taste mentioned above are

not particularly limited. Examples of the substances having a hot taste include red pepper extracts, Japanese horseradish (wasabi) extracts, pepper extracts, ginger extracts, vanilla bean extracts, clove extracts, curry powder extracts, and the like. Ingredients contained in these substances having a hot taste include capsaicin, curcumin, and the like. These substances having a hot taste can be used alone or in admixture of two or more kinds.

The substances having a sour taste mentioned above are not particularly limited. Examples of the substances having a sour taste include citrus-based plant extracts such as lemon, organic acids, and the like. Ingredients contained in these substances having a sour taste include vitamin C, peppermint, citral, citric acid, and the like. These substances having a sour taste can be used alone or in admixture of two or more kinds.

The substances having a pungent taste mentioned above are not particularly limited. Examples of the substances having a pungent taste include tea extracts, algae extracts, soybean extracts, fish extracts, palm extracts, crude drug extracts, and the like. Ingredients contained in these substances having pungent taste include polyphenol compounds, carotenoid compounds, isoflavone compounds, docosahexaenoic acid, eicosapentaenoic acid,

arachidonic acid, saponin, palm oil, vitamin E, linoleic acid, linolenic acid, and the like. These substances having a pungent taste can be used alone or in admixture of two or more kinds.

The substances having a sweet taste mentioned above are not particularly limited. Examples of the substances having a sweet taste include natural or artificial sweeteners. Concrete examples of the substances having a sweet taste include aspartame, saccharin, dulcin, stevioside, acesulfame K, cyclo(sodium cyclamate), aritame, glycyrrhizine, rakan fruit, and the like.

The substances having tastiness mentioned above are not particularly limited. Examples of the substances having tastiness include organic acids, organic bases, acid amides, amino acids, peptides, nucleotides, glutamic acid, sodium glutamate, asparagine, glutamine, theanine, tricolominic acid, ibotenic acid, sodium inosinate, sodium guanylate, and the like.

The substances having a fish odor mentioned above are not particularly limited. Examples of the above substances having a fish odor include fish oil, algae extract oil, and the like. Ingredients contained in these substances having a fish odor include docosahexaenoic acid-containing mixtures, eicosapentaenoic acid-containing mixtures, arachidonic acid-containing mixtures,

trimethylamine-containing mixtures, carotenoid-containing mixtures, and the like. These substances having a fish odor can be used alone or in admixture of two or more kinds.

The substances having a plant odor mentioned above are not particularly limited. Examples of the above substances having a plant odor include tea extracts, algae extracts, soybean extracts, guillate extracts, coffee bean extracts, garlic extracts, crude drug extracts, and the like. Ingredients contained in these substances having a plant odor include polyphenol-containing mixtures, carotenoid-containing mixtures, isoflavone-containing mixtures, docosahexaenoic acid-containing mixtures, eicosapentaenoic acid-containing mixtures, arachidonic acid-containing mixtures, saponin-containing mixtures, palm oil-containing mixtures, caffeine-containing mixtures, vitamin E-containing mixtures, and the like. These substances having a plant odor can be used alone or in admixture of two or more kinds.

The substances having a rotten odor mentioned above are not particularly limited. Examples of the above substances having a rotten odor include aminovaleral, aminovalerianic acid, and the like, which are ingredients for rotten odors in meat, fish, and the like.

The substances having a fermented odor mentioned

above are not particularly limited. Examples of the above substances having a fermented odor include methylmercaptane, ethylmercaptane, methylmercaptopropyl alcohol, ethyl methylmercaptopropionate, butyric acid, and the like, which are contained in soybean paste (miso), soy sauce, cheese, and the like.

The substances susceptible to undergo deterioration mentioned above refers to those substances having a property such that colors inherently owned by the substances or activities such as chemical activity and biological activity are decreased or lost by light, heat, oxygen, or the like.

Examples of the substances susceptible to undergo deterioration mentioned above include vitamins, pigments, perfumes, spices, fish oils, plant oils and derivatives thereof, compositions comprising these substances. These substances susceptible to undergo deterioration may be natural ones or synthesized ones as long as they can be used for foods. In addition, each of the substances susceptible to undergo deterioration may be used alone, or in admixture of two or more kinds.

Examples of the vitamins mentioned above include vitamin A's, carotenoids, vitamin B's, ascorbic acid, vitamin E's, vitamin K, and the like. Examples of the carotenoids include α-carotene, β-carotene, γ-carotene,

lutein, lycopene, canthaxanthin, and the like. Examples of the vitamin E's include α-tocopherol, β-tocopherol, γ-tocopherol, δ-tocopherol, and the like.

Examples of the pigments mentioned above include anthocyanin pigments such as hibiscus pigment, red cabbage pigment, sweet potato pigment, and blueberry pigment; flavonoid pigments such as safflower pigment; carotenoid pigments such as potato pigment, dunaliella pigment, carrot pigment, and pigments derived from palm; chlorella pigment; turmeric pigment; naphthoquinone pigment, and the like.

Examples of the perfumes mentioned above include peppermint oil, beefsteak plant oil, spearmint oil, lavender oil, rosemary oil, cumin oil, clove oil, eucalyptus oil, lemon oil, orange oil, lime oil, rose oil, cinnamon oil, pepper oil, vanilla, ginger oil, and the like.

Examples of the spices mentioned above include spices extracted from capsicum, cardamon, mints, peppers, turmeric, cumin, sage, parsley, oregano, saffron, rosemary, thyme, and the like.

The fish oils are not particularly limited. Examples of the above fish oils include those fish oils extracted from whales, tunas, sardines, mackerels, salmons, and the like.

Examples of the plant oils mentioned above include plant oils extracted from palm, soybean, algae, rapeseeds, peanuts, sesames, coconut palm, and the like.

Examples of the derivatives of the plant oils mentioned above include hydrogenated oils such as palm hardened oil and soybean hardened oil.

As to the mixing proportion of the delipidated egg yolk particles to the functional food material mentioned above, it is desired that the amount of the functional food material in 100 parts by weight of the resulting powder composition is 5 parts by weight or more, preferably 10 parts by weight or more, from the viewpoints of increasing the content of the functional food material in the resulting powder composition and increasing economic advantages, and that the amount of the food functional material is 60 parts by weight or less, preferably 50 parts by weight or less, from the viewpoint of increasing the flowability.

Incidentally, when the delipidated egg yolk particles are mixed with the functional food material, an emulsifier may be further added in an appropriate amount from the viewpoints of improving the flowability and improving the dispersibility to water. The above emulsifier may be any kind as long as it can be used for foods. Representative examples of the emulsifier mentioned above include

glycerol fatty acid esters, polyglycerol fatty acid esters, sucrose fatty acid esters, sorbitan fatty acid esters, propylene glycol fatty acid esters, lecithin, enzymatically decomposable lecithin, and the like. The amount of the emulsifier mentioned above cannot be absolutely determined because it differs in accordance with the kind of the emulsifier. For instance, in a case where a glycerol fatty acid ester is used as an emulsifier, the dispersibility to water can be improved by using the glycerol fatty acid ester in a proportion of 0.01 to 0.5 parts by weight, based on 100 parts by weight of the mixture (calculated as solid ingredients) of the delipidated egg yolk particles and the functional food material.

Further, in the present invention, when the delipidated egg yolk particles mentioned above are mixed with the functional food material, as occasion demand, there may be appropriately added proteins such as soybean protein and milk protein; carbohydrates such as dextrin; and materials such as silica, calcium tertiary phosphate, calcium of egg shells, and minerals of milk sera. From the viewpoint of increasing oxidation stability, there may be appropriately added as antioxidants, for instance, lecithin, tea extracts, t-butylhydroxytoluene, t-butylhydroxyanisole, tocopherol, ethoxyquin, and the

like.

The method for mixing the delipidated egg yolk particles and the functional food materials mentioned above, and ingredients such as other materials as occasion demands are not particularly limited, as long as these ingredients are homogeneously dispersed.

Next, the resulting mixture is dried under reduced pressure. One of the large feature in the present invention also resides in the employment of the procedure of drying the resulting mixture under reduced pressure. When the procedure as described above is carried, the functional food material is sufficiently impregnated into the pores of the surfaces of the delipidated egg yolk particles, as compared with those cases obtainable by other drying means.

Therefore, the delipidated egg yolk particles impregnated with the functional food material are less likely to be sticky and has excellent flowability.

An example of a method for drying the mixture mentioned above includes a method comprising drying the mixture under reduced pressure using a vacuum kneader, or the like. The pressure during the drying under reduced pressure is not particularly limited, and it is preferable that the pressure is usually 100 mmHg or less. In addition, the temperature during drying under reduced

pressure is not particularly limited, and it is preferable that the temperature is usually 25° to 80°C or so.

Incidentally, when drying under reduced pressure, it is preferable that drying is carried out with stirring the mixture mentioned above, from the viewpoint of homogeneously mixing the functional food material and the delipidated egg yolk particles, thereby facilitating the impregnation into the pores on the surfaces.

The drying of the mixture mentioned above is thus carried out. It is desired that drying is carried out to a point such that the water content contained in the mixture mentioned above is usually 10% by weight or less, preferably 5% by weight or less, in order to impart excellent flowability in the resulting powder composition.

Thus, there can be obtained a powder composition comprising particles in which the functional food material mentioned above is impregnated into the pores of the surfaces of the delipidated egg yolk particles.

It is desired that the average particle size of the particles constituting the powder composition of the present invention (as determined by observation with electron microscope) is usually from about 1 to about 100 μm, preferably from about 20 to about 60 μm, from the viewpoint of excellent dispersibility.

The powder composition of the present invention has

excellent flowability, and gives excellent sense of fluidity when packed in a sack. The angle of repose of the above powder composition is 60° or less, preferably 50° or less, as determined by an analyzer for determining an angle of repose by Miwa-type cylindrical rotation method (manufactured by Tsutsui Rikagaku Kikai K.K.) under the conditions of a relative humidity of 40% and a temperature of 25°C, with proviso that the measurement is taken by adjusting the water content of the powder composition to 5 ± 2% (determined by Karl Fischer's water content analyzer).

Since the powder composition of the present invention has the above angle of repose, its flowability is excellent, and its method for production is simple. Also, since the functional food material can be contained at a high concentration, there can be exhibited the effects that bacterial contamination or deterioration of the substances being susceptible to undergo oxidation deterioration is prevented, so that the properties of the functional food material are made stable for a long period of time.

Since the powder composition of the present invention has excellent flavors and palatabilities, is stable, and has excellent flowability, the powder composition can be widely used as food materials, and the like. The powder

composition of the present invention may be, for instance, directly eaten in an appropriate amount with a spoon, or the like, or it may be added to a food, or the like. In addition, the powder composition may be eaten after being processed into baked confectionery such as cookies and biscuits, bread, fried products, curry, stew, ice cream, tablets, preparations, and the like.

The present invention will be described in further detail on the basis of the working examples, without intending to limit the present invention to these examples.

Preparation Example 1

To 100 kg of egg yolk powder was added 2000 liter of ethanol, and the mixture was stirred with a homomixer at 40°C for 30 minutes. The resulting mixture was filtered with a flat plate-type filtration apparatus using a filter paper. To the resulting filtration residue was added 200 kg of deionized water, and mixed. Thereafter, the mixture was dried with a spray-dryer (manufactured by Ohgawara Kakoki under the trade name of Model "DC16", inlet: 140°C, outlet: 75°C), whereby giving 32 kg of delipidated egg yolk particles which were porous, having a large number of pores on the particle surface. The pores were confirmed with SEM. The pore size was such that the

diameter was about 0.1 to about 10 μm. In the following Preparation Examples 2 to 4, the pores were similarly confirmed with SEM.

Preparation Example 2

To 100 kg of egg yolk powder was added 2000 liter of ethanol, and the mixture was stirred with a homomixer at 40°C for 30 minutes. The resulting mixture was filtered with a flat plate-type filtration apparatus using a filter paper. To the resulting filtration residue was added 100 kg of deionized water, and mixed. Thereafter, the mixture was dried with the spray-dryer in the same manner as in Preparation Example 1, whereby giving 32 kg of delipidated egg yolk particles which were porous, having a large number of pores (size: about 0.1 to about 10 μm) on the particle surface.

Preparation Example 3

To 100 kg of egg yolk powder was added 4000 liter of ethanol, and the mixture was stirred with a homomixer at 40°C for 30 minutes. The resulting mixture was filtered with a flat plate-type filtration apparatus using a filter paper. To the resulting filtration residue was added 300 kg of deionized water, and mixed. Thereafter, the mixture was dried with the spray-dryer in the same manner

as in Preparation Example 1, whereby giving 31 kg of delipidated egg yolk particles which were porous, having a large number of pores (size: about 0.1 to about 10 μm) on the particle surface.

Preparation Example 4

To 100 kg of egg yolk powder was added 1000 liter of ethanol, and the mixture was stirred with a homomixer at 40°C for 30 minutes. The resulting mixture was extracted with a rotatable solid-liquid separator, to give an extraction residue. To the resulting extraction residue was added 400 kg of tap water, and mixed. Thereafter, the mixture was dried with the spray-dryer in the same manner as in Preparation Example 1, whereby giving 34 kg of delipidated egg yolk particles which were porous, having a large number of pores (size: about 0.1 to about 10 μm) on the particle surface.

Example 1

In 8 kg of a soybean oil was homogeneously dispersed 5.5 kg of a tea extract (polyphenol content: 78% by weight, caffeine content: 9% by weight), and the resulting dispersion was added to 10 kg of the delipidated egg yolk particles obtained in Preparation Example 1. The mixture was stirred at 30°C for 50 minutes with a vacuum kneader

(manufactured by Kajiwara Kogyo K.K. under the trade name of KDV-5E; 30 mmHg), so that the dispersion was dispersed and impregnated thereinto, to give 23.5 kg of a powder composition (average particle size: 40 μm, water content: 4.2% by weight). The resulting powder composition had excellent flowability (evaluated with respect to sense of fluidity when packed in a sack, the same for the following Examples), was free from odor and bitter taste distinctively owned by the tea extract, and had excellent flavor.

Example 2

In 12 kg of ethanol was homogeneously dispersed 8 kg of a tea extract (polyphenol content: 78% by weight, caffeine content: 9% by weight), and the resulting dissolved dispersion was added to 10 kg of the delipidated egg yolk particles obtained in Preparation Example 1. The mixture was stirred at 30°C for 50 minutes with a vacuum kneader (30 mmHg) in the same manner as in Example 1, so that the dispersion was dispersed and impregnated thereinto, to give 18 kg of a powder composition (average particle size: 40 μm, water content: 3.4% by weight). The resulting powder composition had excellent flowability, was free from odor and bitter taste distinctively owned by the tea extract, and had excellent flavor.

Example 3

To 10 kg of the delipidated egg yolk particles obtained in Preparation Example 2 was added 2 kg of a 30% β-carotene containing plant oil suspension having an distinctive odor. The mixture was stirred at 30°C for 30 minutes with a vacuum kneader (30 mmHg) in the same manner as in Example 1, to give 12 kg of a powder composition (average particle size: 34 μm, water content: 5.1% by weight). The resulting powder composition had excellent flowability, was free from odor distinctively owned by the β-carotene, and had excellent flavor.

Example 4

In 8 kg of a salad oil was suspended 4 kg of soybean isoflavone, and 10 kg of the delipidated egg yolk particles obtained in Preparation Example 2 was added to the resulting suspension. The mixture was stirred at 30°C for 30 minutes with a vacuum kneader (30 mmHg) in the same manner as in Example 1, to give 22 kg of a powder composition (average particle size: 51 μm, water content: 4.7% by weight). The resulting powder composition had excellent flowability, was free from bitter taste distinctively owned by the soybean isoflavone, and had excellent flavor.

Example 5

To 10 kg of the delipidated egg yolk particles obtained in Preparation Example 2 was added 2 kg of a ginger oil. The mixture was stirred at 25°C for 30 minutes with a vacuum kneader (30 mmHg) in the same manner as in Example 1, to give 12 kg of a powder composition (average particle size: 38 μm, water content: 5.3% by weight). The resulting powder composition had excellent flowability, was free from odor distinctively owned by the ginger oil, and had excellent flavor.

Example 6

To 10 kg of the delipidated egg yolk particles obtained in Preparation Example 1 was added 3 kg of a fish oil (DHA content: 25% by weight). The mixture was stirred at 30°C for 1 hour with a vacuum kneader (30 mmHg) in the same manner as in Example 1, to give 12.8 kg of a powder composition (average particle size: 46 μm, water content: 5.6% by weight). The resulting powder composition had excellent flowability, was free from fish odor, and had excellent flavor.

Comparative Example 1

To 10 parts by weight of the egg yolk powder was added 100 parts by weight of ethanol, and the mixture was

stirred with a homomixer at 30°C for 30 minutes. The resulting mixture was filtered with a filter press, and the resulting filtration residue was dried with a rotatable vacuum dryer, and thereafter classified with 40 mesh sieves. To 10 kg of the resulting delipidated egg yolk powder was added 3 kg of a fish oil (DHA content: 25% by weight), and the mixture was stirred with a supermixer so as to have a homogeneous state, to give 13 kg of powdery fats and oils. The resulting powdery fats and oils had slight fish odor and poor flowability. In addition, the delipidated egg yolk before adding the fish oil was examined by SEM. The surface had a shrinking state, and no pores were found thereon.

Comparative Example 2

To 10 parts by weight of the egg yolk powder was added 100 parts by weight of ethanol, and the mixture was stirred with a homomixer at 30°C for 60 minutes. The resulting mixture was filtered with a filter press, and the resulting filtration residue was dried with a rotatable vacuum dryer. To 10 kg of the resulting delipidated egg yolk powder was added a dispersion obtained from uniformly dispersing 5.5 kg of a tea extract (polyphenol content: 78% by weight, caffeine content: 9% by weight) in 8 kg of a soybean oil, and the mixture was

stirred with a supermixer so as to have a homogeneous state, to give 23.5 kg of a powder (average particle size: 60 μm, water content: 5.9% by weight). The resulting powder composition had poor flowability. In addition, there was slightly found odor or bitter taste distinctively owned by the tea extract. The delipidated egg yolk powder before adding the tea extract was observed by SEM. As a result, the delipidated egg yolk powder had an irregular shape, and no pores were found thereon.

Test Example 1

An angle of repose for each 500 g of the powdery fats and oils obtained in Comparative Example 1 and the powder composition obtained in Example 6 was measured by an analyzer for determining an angle of repose by Miwa type cylindrical rotation method (manufactured by Tsutsui Rikagaku Kikai K.K.). The angle of repose for the powdery fats and oils obtained in Comparative Example 1 was 75°, and the angle of repose for the powder composition obtained in Example 6 was 50°. The water contents in the sample were 5.2% (Comparative Example 1) and 5.6% (Example 6), respectively.

Test Example 2

Panelists consisting of 5 each of male and female

normal individuals of an age of 24 to 34 years old were subjected to sensory examination for "bitterness" with a tea extract, the powder compositions obtained in Examples 1 and 2, and powder obtained in Comparative Example 2 by placing 20 mg of each powder on the tongue. The evaluation criteria are as follows.

Evaluation Scores

0	No bitterness;
1	Slight bitterness;
2	Little bitterness;
3	Some bitterness;
4	Marked bitterness; and
5	Strong bitterness.

The value obtained by dividing the total sum of the evaluation scores for "bitterness" for each individual panelists by the total number of the panelists (10 persons) was defined as sensory evaluation for "bitterness".

Results

Sample	Evaluation Value for "Bitterness"
Tea Extract only	4.8

Powder Composition of Example 1	1.2
Powder Composition of Example 2	1.8
Powder of Comparative Example 2	3.8

It is clear from the above results that the powder compositions of Examples 1 and 2 of the present invention are powder compositions in which the exhibition of the undesirable flavor (bitterness) owned by the tea extract is suppressed.

Test Example 3

The powdery fats and oils containing a fish oil obtained in Comparative Example 1, the powder composition containing a fish oil obtained in Example 6, and the powdery fats and oils previously prepared by adding 3 kg of a fish oil (DHA content: 25% by weight) to 10 kg of cornstarch each in an open system were respectively stored at 60°C in dark place. The POV measurement and the sensory examination were carried out with the passage of time. The mixture of cornstarch with a fish oil caused an unpleasant odor after 3 days, of which POV reached 80 meq./kg. The mixture of the powdery fats and oils obtained in Comparative Example 1 with a fish oil was stable after 10 days, but caused a slight unpleasant odor

after 30 days, of which POV became 30 meq./kg. On the other hand, the powder composition containing a fish oil obtained in Example 6 caused no unpleasant odor even after 30 days, of which POV was as low as 0.5 meq./kg, showing no changes from the time of preparation.

INDUSTRIAL APPLICATION

The powder composition of the present invention has excellent flowability and little stickiness, and the functional food material can be contained therein at a high concentration, so that the deterioration of the substances susceptible to undergo deterioration by light, heat, oxygen, or the like is prevented, whereby making the flavor of the substance having undesirable flavor better, and the properties of the functional food material are made stable for a long period of time. Therefore, the powder composition of the present invention can be suitably used for baked confectionery such as cookies and biscuits, bread, fried products, curry, stew, baby foods, tablets, preparations, capsules, and the like. In addition, the powder composition of the present invention may directly be eaten in an appropriate amount.

CLAIMS

1. A powder composition, characterized in that the powder composition comprises delipidated egg yolk particles and a functional food material, the functional food material being impregnated in pores of the delipidated egg yolk particles.

2. The powder composition according to claim 1, wherein an angle of repose is 60° or less, as measured under the conditions of the water content of 5 ± 2%, relative humidity of 40%, and a temperature of 25°C.

3. The powder composition according to claim 1, wherein the average particle size is from 1 to 100 μm.

4. The powder composition according to claim 1, wherein the powder composition comprises 5 to 60% by weight of the functional food material.

5. The powder composition according to claim 1, wherein the functional food material is a substance having a undesirable flavor, or a substance susceptible to undergo deterioration with light, heat or oxygen.

6. A method for preparing a powder composition characterized by:

(A) mixing a delipidated egg yolk with water, spray-drying the resulting mixture, to prepare porous, delipidated egg yolk particles having pores on surfaces thereof; and

(B) mixing the resulting delipidated egg yolk particles with a functional food material, and drying the resulting mixture under reduced pressure.

7. The method for preparing a powder composition according to claim 6, wherein the mixture is dried under reduced pressure with stirring in the step (B).

8. A food comprising the powder composition according to any one of claims 1 to 5.

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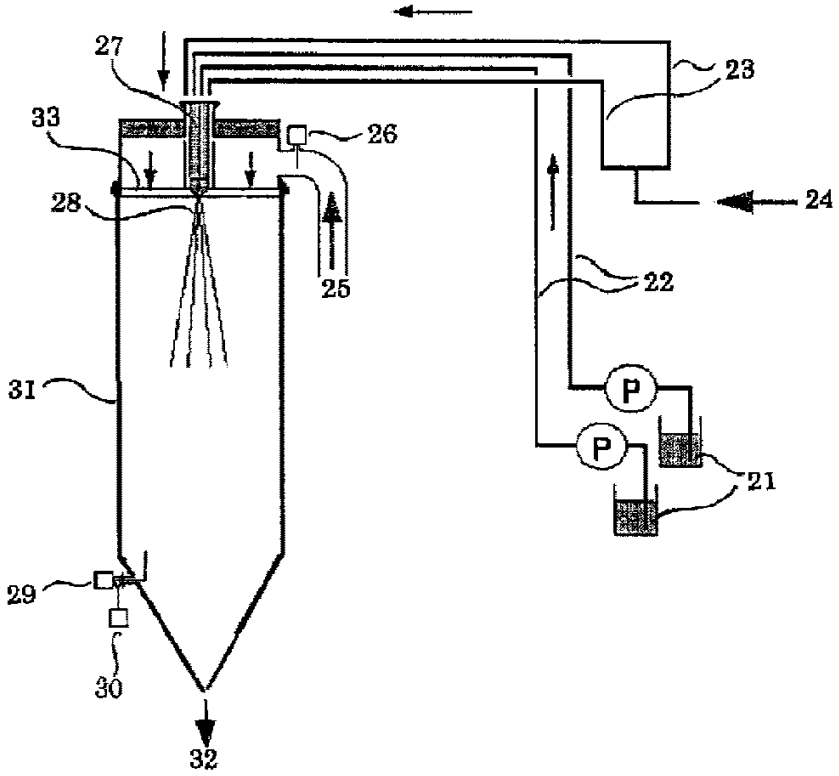
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(54) Titre : MICROORGANISME SECHE PAR PULVERISATION
(54) Title: DRIED MICROORGANISM CELL PRODUCT BY SPRAY-DRYING



(57) Abrégé/Abstract:
An object of the present invention is to provide a method for drying the liquid of microorganism cells where, in a manufacturing step of a dried microorganism cell product or of a composition such as pharmaceutical or food containing the same extinction or

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(57) Abrégé(suite)/Abstract(continued):
damage of microorganism cells is suppressed as much as possible and survival rate is able to be highly retained and another object is to provide a dried microorganism cell product in a single micron size having many cell numbers per unit weight and being easily made into pharmaceutical or food.
The present invention relates to a method for the manufacture of a dried microorganism cell product, characterized in that, sprayed liquid droplets in a single micron size are dried with drying wind and also to a dried microorganism cell product in a single micron size.

Abstract

An object of the present invention is to provide a method for drying the liquid of microorganism cells where, in a manufacturing step of a dried microorganism cell product or of a composition such as pharmaceutical or food containing the same, extinction or damage of microorganism cells is suppressed as much as possible and survival rate is able to be highly retained and another object is to provide a dried microorganism cell product in a single micron size having many cell numbers per unit weight and being easily made into pharmaceutical or food.

The present invention relates to a method for the manufacture of a dried microorganism cell product, characterized in that, sprayed liquid droplets in a single micron size are dried with drying wind and also to a dried microorganism cell product in a single micron size.

Description

DRIED MICROORGANISM CELL PRODUCT BY SPRAY-DRYING

Technical Field

The present invention relates to a method for the manufacture of a dried microorganism cell product using spray drying, to a dried microorganism cell product obtained by the said manufacturing method and to a composition such as pharmaceutical or food containing the said dried microorganism cell product.

Background of the Invention

With regard to a drying method in the manufacturing step of pharmaceutical and food, freeze-drying or vacuum freeze-drying has been so much used. Freeze-drying is a method where drying is carried out using liquid nitrogen or the like at the temperature of as low as from about -20°C to about -160°C and vacuum freeze-drying is a method where drying is carried out at about 35°C or lower under the pressure of from about 50 to about 400 hPa.

However, when freeze-drying or vacuum freeze-drying is adopted as a drying method in the manufacturing step for microorganism cells of lactic acid bacteria, yeast, etc. or for a composition such as pharmaceutical or food containing the same, there is a disadvantage that the microorganism cells are killed or damaged during the drying. That is because long time is needed until reaching the freezing temperature in freeze-drying or vacuum freeze-drying and the microorganism is damaged by

metabolites of the microorganism produced during that period or by a freezing process. Especially in the case of vacuum freeze-drying, the drying speed is very slow and, if water in the pharmaceutical or food is to be completely removed, the drying time becomes far longer whereby the above-mentioned problem becomes more significant.

Moreover, in carrying out freeze-drying or vacuum freeze-drying, equipment of a very big scale is necessary and much cost is required for investment of the equipment.

Further, when freeze-drying or vacuum freeze-drying is adopted as a drying method, it is difficult to manufacture by means of continuous steps and, therefore, manufacturing steps become troublesome. Furthermore, after freeze-drying or vacuum freeze-drying, additional steps such as grinding and homogenization are necessary whereby manufacturing steps become many and extinction of the microorganism during the steps becomes a problem.

Problems as such have been pointed out for freeze-drying or vacuum freeze-drying.

On the other hand, with regard to a drying method, spray-drying has been known besides freeze-drying or vacuum freeze-drying. Spray-drying is a method where liquid is made into liquid droplets by a device for preparing fine particles and the liquid droplets are contacted with dry wind of a relatively high temperature to dry by evaporation of moisture.

However, in the conventional spray-drying, temperature of the wind for drying is high and microorganism is killed by the heat of the drying wind whereby that has been said to be unsuitable for the manufacture of pharmaceutical or food

containing living cells. When temperature of the drying wind is made low for solving such a problem, it is not possible to give a well-dried microorganism cell product whereby there are problems that both yield and stability decrease.

Disclosure of the Invention

An object of the present invention is to provide a method for drying the liquid of microorganism cells where, in a manufacturing step of a dried microorganism cell product or of a composition such as pharmaceutical or food containing the same, extinction or damage of microorganism cells is suppressed as much as possible and survival rate is able to be highly retained.

Another object of the present invention is to provide a dried microorganism cell product in a single micron size having many cell numbers per unit weight and being easily made into pharmaceutical or food.

Still another object of the present invention is to provide a method for the manufacture of a microorganism cell composition where the manufacturing steps can be greatly simplified and also to provide a device concerning the said manufacturing method.

The present inventors have carried out intensive investigations for achieving the above-mentioned objects and obtained the finding that, when spray-dried liquid droplets of a single micron size are dried by drying wind, problems in the conventional spray-drying can be solved.

Thus, sprayed liquid droplets formed by the conventional spray-drying devices are about 10-40 μm while, when they are in sprayed liquid droplets of as small as a single micron size,

surface area per unit weight of the sprayed liquid droplets becomes bigger whereby contact with drying wind proceeds very efficiently. Accordingly, when drying is carried out by drying wind of the temperature which is in the same degree as that in the conventional spray-drying, the time required for drying the microorganism cell liquid becomes shorter and extinction or damage of the microorganism cells can be suppressed as much as possible. Further, even when the temperature of drying wind is made lower than the temperature of drying wind in the conventional spray-drying, a sufficient drying is possible without deteriorating the yield or stability and, furthermore, since the temperature of drying wind is low, extinction or damage of the microorganism cells due to heat of drying wind can be suppressed as much as possible.

The present inventors have further found that the dried microorganism cell product obtained by drying of sprayed liquid droplets in a single micron size by drying wind have a small particle size and contain particles of a single micron size. A dried microorganism cell product having a small particle size has advantages that the pressure to be applied to the microorganism cells upon compressive molding, etc. is small and static electricity is hardly generated whereupon it is easily made into pharmaceutical or food in a preparation form such as tablets.

Thus, the present invention relates to:

(1) A dried microorganism cell product in a single micron size;

(2) The dried microorganism cell product mentioned in the above (1), wherein viable cell count is from 1.0×10^5 to 2.0

$\times 10^{12}$ CFU/g;

(3) A dried microorganism cell product in which viable cell count is from 1.0×10^{11} to 2.0×10^{12} CFU/g;

(4) The dried microorganism cell product mentioned in the above (1) to (3), wherein the microorganism is bifidobacteria, lactobacillus, lactococci, sporogenous lactic acid bacteria, saccharification bacteria, yeast, koji mold, actinomycetes, *Bacillus toyoi*, *B. licheniformis*, butyric acid bacteria, acetic acid bacteria or amino acid fermentation bacteria;

(5) A dried microorganism cell product, characterized in that, the dried microorganism cell product mentioned in the above (1)-(4) is further coated or masked;

(6) A method for the manufacture of the dried microorganism cell product mentioned in the above (1)-(5), characterized in that, sprayed liquid droplets in a single micron size are dried with drying wind;

(7) The method for the manufacture of the dried microorganism cell product according to the above (6), wherein the sprayed liquid droplets in a single micron size are formed by a four-passage nozzle;

(8) The method for the manufacture of the dried microorganism cell product according to the above (6) or (7), wherein the temperature of drying wind is 5~150°C at the inlet of a drying chamber;

(9) A method for the manufacture of the dried microorganism cell product mentioned in the above (5), characterized in that, a liquid coating agent or masking agent is sprayed together with a microorganism cell liquid to form sprayed liquid droplets and the said sprayed liquid droplets

are dried with drying wind;

(10) The method for the manufacture of the dried microorganism cell product according to the above (9), wherein the microorganism cell liquid is supplied from one liquid passage in a four-passage nozzle having two liquid passages and two gas passages, a liquid coating agent or masking agent is supplied from another liquid passage, compressed gas is supplied from the two gas passages and the resulting sprayed liquid droplets are dried by a drying wind;

(11) A method for the manufacture of a microorganism cell composition, characterized in that, a step where a fluidized layer granulation using a powder and a binder and a drying step where dried microorganism cell product of a single micron size is obtained by spray-drying are carried out in the same container;

(12) A device, characterized in that, a step where a fluidized layer granulation using a powder and a binder and a drying step where dried microorganism cell product of a single micron size is obtained by spray-drying are carried out in the same container;

(13) A microorganism cell composition, characterized in that, a dried microorganism cell product of a single micron size is adhered to granules comprising a powder and a binder;

(14) Pharmaceutical or food containing the dried microorganism cell product mentioned in the above (1)-(5) or the microorganism cell composition mentioned in (13); and

(15) Liquid droplets of a single micron size containing microorganism cells.

The present invention further relates to:

(1) A dried microorganism cell product of a single micron size where sprayed liquid droplets of a single micron size are dried by drying warm wind;

(2) The dried microorganism cell product according to the above (1), wherein the sprayed liquid droplets of a single micron size are formed by a four-passage nozzle;

(3) The dried microorganism cell product according to the above (1) or (2), wherein the inlet temperature of the drying warm wind of the drying chamber is 5-150°C;

(4) The dried microorganism cell product according to the above (1) to (3), wherein they are coated or masked;

(5) The dried microorganism cell product according to the above (1) to (4), wherein the sprayed liquid droplets are formed by spraying a liquid coating agent or masking agent and a microorganism cell liquid at the same time;

(6) The dried microorganism cell product according to the above (1) to (5), wherein the microorganism cell liquid is supplied from one liquid passage in a four-passage nozzle having two liquid passages and two gas passages, a liquid coating agent or masking agent is supplied from another liquid passage, compressed gas is supplied from the two gas passage and the resulting sprayed liquid droplets of a single micron size are dried by a warm drying wind;

(7) The dried microorganism cell product according to the above (1) to (6), wherein the microorganism is bifidobacteria, lactobacillus, lactococci, sporogenous lactic acid bacteria, saccharification bacteria, yeast, koji mold, actinomycetes, *Bacillus toyoi*, *B. licheniformis*, butyric acid bacteria, acetic acid bacteria or amino acid fermentation bacteria;

(8) The dried microorganism cell product according to the above (1) to (7), wherein the viable cell count is from 1×10^{11} to 2.0×10^{12} CFU/g; and

(9) Pharmaceutical or food containing the dried microorganism cell product mentioned in the above (1) to (8).

Brief Description of the Drawings

Fig. 1 shows an internal structure of a nozzle edge part in a spray-drying device having a four-passage nozzle.

Fig. 2 shows a rough sketch of a spray-drying device having a four-passage nozzle.

Fig. 3 shows changes in viable cell count during the acid-resistance test of a dried microorganism cell product subjected to an enteric coating.

Fig. 4 shows a rough sketch of a device which is characterized in that a step where a fluidized layer granulation using a powder and a binder and a drying step where dried microorganism cell product of a single micron size is obtained by spray-drying are carried out in the same container in accordance with the present invention.

Explanation of symbols:

1, 2 gas passage wherefrom compressed gas is supplied

3, 4 liquid passage wherefrom liquid containing a substance to be dried is supplied

5 fluidized surface of fluid

6 focus of collision

7 sprayed liquid droplet

21 microorganism cell liquid, coating agent or masking agent

22 passage for liquid

23 passage for gas

24 inlet for compressed air

25 inlet for drying wind

26 inlet thermometer

27 device for preparing fine particles

28 four-passage nozzle

29 outlet thermometer

30 pressure gage for inner area of drying chamber

31 drying chamber

32 outlet for dried microorganism cell product

33 rectification device

41 main body of device

42 fluidized bed

43 bug filter

44 microorganism cell liquid

45 binder

46 nozzle for spraying of microorganism cell liquid

47 nozzle for spraying of binder

48 powder

49 gas for fluidization

Best Mode for Carrying Out the Invention

The dried microorganism cell product of the present invention usually means each dried microorganism cell or aggregate of dried microorganism cell product.

With regard to the dried microorganism cell product according to the present invention or the dried microorganism cell product contained in the composition such as

pharmaceutical or food according to the present invention, anything may be within coverage of the present invention so far as the dried microorganism cell product having a particle size of a single micron size are contained. Accordingly, even such a case where the above-mentioned dried microorganism cell product comprises a mixture of dried microorganism cell product having a particle size of a single micron size and dried microorganism cell product having a particle size of not less than a single micron size such as the case where a mean value of the particle size is a single micron size is also within coverage of the present invention.

Here, the term "single micron" means a value of 1-10 μm when the first decimal place is rounded.

There is no particular limitation for the microorganism used in the present invention and its examples are bifidobacteria such as *Bifidobacterium bifidum, B. longum, B. breve, B. adrecentis, B. infantis, B. pseudolongum* and *B. thermophilum*; lactobacillus such as *Lactobacillus acidophilus, L. casei, L. gasseri, L. plantalum, L. delbrueckii* subsp. *bulgaricus* and *L. delbrueckii* subsp. *lactis*; lactococci such as *Leuconostoc mecenteroides, Streptococcus (Enterococcus) faecalis, Streptococcus (Enterococcus) faecium, Streptococcus (Enterococcus) hirae, Lactococcus lactis* and *Streptococcus thermophilus*; sporogenous lactic acid bacteria such as *Bacillus coagulans*; saccharification bacteria such as *Bacillus subtilis, Bacillus mesentericus* and *Bacillus polyfermenticus*; yeasts such as *Saccharomyces cerevisiae* and *Candida*; koji molds such as *Aspergillus oryzae, A. niger* and *A. sojae*; actinomycetes such as *Streptomyces*; butyric acid bacteria such as *Bacillus toyoi*,

B. licheniformis and *Clostridium butyricum*; acetic acid bacteria such as *Acetobacter*; amino acid fermentation bacteria such as *Corynebacterium*; and other useful microorganisms.

The above-mentioned microorganism cells can be prepared by incubation under the known conditions or the conditions similar thereto. For example, in the case of lactic acid bacteria, one or more of the above-mentioned lactic acid bacteria is/are incubated in a liquid medium containing glucose, yeast extract, peptone, etc. usually at about 25-45°C for about 4-24 hours and the cells are collected from the incubated liquid and washed to give the wet cells.

The microorganism cells may be a processed product of the above-mentioned microorganism cells. Examples of the process are extraction with an appropriate solvent, etc. Specific examples are yeast extract which is an extract of yeast with hot water, etc.

In the method for the manufacture of a dried microorganism cell product in accordance with the present invention, the above-mentioned microorganism cells are firstly dissolved in a solvent to prepare a microorganism cell liquid. With regard to the solvent, although that which has been publicly known in the art may be used, water is preferred. If desired, ethyl alcohol or the like may be added thereto. When ethyl alcohol or the like is added, ethyl alcohol or the like is firstly vaporized and then water is vaporized whereby a stepwise drying is possible.

The microorganism cell liquid may be a suspension. With regard to the solvent, known one may be used as mentioned above although water or aqueous solution where ethyl alcohol or the

like is added to water is preferred. In the preparation of a suspension, a suspending agent may be used. With regard to a suspending agent, known ones such as sodium alginate or methyl cellulose may be used.

A protective agent may be added to the above microorganism cell liquid.

The protective agent may be that which has been commonly used in the art and its examples are vitamins such as ascorbic acid; amino acids such as glutamine, glutamic acid, L-cysteine, glycine, phenylalanine, serine or threonine; saccharides or sugar alcohols such as glucose, fructose, sucrose, maltose, mannitol or maltitol; polysaccharides such as oligosaccharide, cyclodextrin or dextrin; fats such as higher fatty acids obtained from rapeseed, soybean, peanut, etc.; proteins such as those obtained from cow's milk, soybean, etc. and degraded proteins such as peptide; inorganic salts such as magnesium sulfate; and others such as sucrose fatty acid ester, malic acid, nucleic acids, yeast extract, skim milk, peptone, gelatin, tannin, etc.

With regard to the protective agent, one of the above-mentioned substances may be used solely or any two or more thereof may be used jointly. Incidentally, it is preferred that the said protective agent is added in an amount of about 0.1-5.0-fold or, preferably, about 0.5-3.0-fold of the weight of the wet microorganism cells.

Additives which have been commonly used in the art such as excipient, binder, disintegrating agent, antistatic agent, etc. may be further added to the above microorganism cell liquid in a common compounding ratio.

With regard to the excipient, there may be used saccharides such as lactose, granulated sugar and corn starch; sugar alcohols such as mannitol; and cellulose such as natural cellulose, crystalline cellulose, etc. and cellulose derivatives such as hydroxycellulose. Examples of the crystalline cellulose are water-insoluble cellulose in white powder prepared by subjecting natural cellulose to, for example, an acidic treatment so that network molecular structure is made fine to some extent, etc. A mixture of crystalline cellulose with carmellose or carmellose sodium may be also exemplified.

Examples of the binder are hydroxypropyl cellulose, hydroxypropyl methylcellulose, methylcellulose, dextrin and α-starch.

Examples of the disintegrating agent are carmellose calcium, cross-linked product (AcDiSol) of carmellose, carmellose sodium, etc., cross-linked product (Plasdone) of polyvinylpyrrolidone, etc., corn starch and lowly substituted hydroxypropyl cellulose.

Examples of the antistatic agent are Syloid, talc and Aerosil.

Then the above-mentioned microorganism cell liquid is subjected to a spray-drying in the method for the manufacture of a dried microorganism cell product according to the present invention. With regard to a spray-drying device used for the said spray-drying, a spray-drying device equipped with a device giving fine particles being able to form sprayed liquid droplets of a single micron size is preferred. This is because, when sprayed liquid droplets having very small particle size are prepared, surface area per unit weight of the sprayed liquid

droplets becomes bigger, contact with drying wind is done efficiently whereby extinction or damage of the microorganism by heat of the drying wind can be suppressed as much as possible.

Here, sprayed liquid droplets of a single micron size mean that the particle size of a sprayed liquid droplet is 1-10 μm when its first decimal place is rounded off.

A specific example of the spray-drying device is a spray-drying device where a device for preparing fine particles is a two-passage nozzle or a four-passage nozzle utilizing the force of rotary atomizer (rotary disk), compressing nozzle or compressed gas.

In the present invention, any of the above-mentioned spray-drying devices may be used regardless of the type but, in view of the fact that fine sprayed liquid droplets are able to be prepared, the use of a spray-drying device having a four-passage nozzle is preferred. The said spray-drying device may be that which has been known *per se*.

Structure of the four-passage nozzle in a spray-drying device having a four-passage nozzle is that, when a gas passage and a liquid passage comprise a system, they are symmetrically installed at the nozzle edge in two systems and a slope which is a fluidized surface of fluid is installed at a nozzle edge.

An embodiment of the structure of the four-passage nozzle will be illustrated in more detail by referring to Fig. 1. In a nozzle edge of the four-passage nozzle, the microorganism cell liquid coming out from the liquid passage 3 or 4 as if sprung out therefrom is thinly extended on a fluidized surface of fluid 5 by a high-speed gas flow coming out from the gas passage 1 or 2 and the extended liquid is made into fine particles by shock

wave generated at the focus of collision 6 at the front end of the nozzle edge whereupon sprayed liquid droplets 7 of a single micron size are formed.

As such, the preferred four-passage nozzle is that which is in an externally mixing system where compressed gas and liquid are focused to a point from both sides toward the focus of collision of the front end of the nozzle edge. This is because, in such a system, there is no clogging of the nozzle whereby it is possible to spray for a long period.

With regard to the compressed gas, it is possible, for example, to use air, carbon dioxide gas, nitrogen gas, argon gas and other inert gas. Especially when a thing which is apt to be oxidized is spray-dried, it is preferred to use inert gas such as nitrogen gas or argon gas.

Pressure of the compressed gas is about 1-15 kg weight/cm^2 or, preferably, about 3-8 kg weight/cm^2.

Amount of the gas at the nozzle per 1 mm of the nozzle edge is about 1-100 L/minute, preferably about 5-50 L/minute or, more preferably, about 10-20 L/minute.

An embodiment of the spray-drying device having a four-passage nozzle is shown in Fig. 2. When an embodiment of the spray-drying according to the present invention is illustrated using Fig. 2, the microorganism cell liquid 21 is sprayed from the four-passage nozzle 28 as illustrated hereinabove by referring to Fig. 1. In a drying chamber 31, the said spray-dried liquid droplets are contacted with drying wind sent via a rectification device 33 from a drying wind inlet 25 whereupon moisture is evaporated to give a dried microorganism cell product.

Temperature of the drying wind at the inlet of the drying chamber (hereinafter, referred to as "inlet temperature") is about 2-400°C, preferably about 5-250°C or, more preferably, 5-150°C. Even when the inlet temperature is as high as about 200-400°C, temperature of the thing to be dried does not become so high due to heat of vaporization of water and, further, extinction and damage of viable cells can be suppressed as much as possible when residence time in the drying chamber is made short.

Temperature of the drying wind at the outlet of the drying chamber (hereinafter, referred to as "outlet temperature") is about 0-120°C, preferably about 5-90°C or, more preferably, about 5-70°C.

In the spray-drying device as shown in Fig. 2, the inlet temperature is the temperature measured by a thermometer at the inlet (26) while the outlet temperature is the temperature measured by a thermometer at the outlet (29).

The drying chamber may be vacuated. As a result of vacuation, there is an advantage that a drying efficiency is improved and drying time becomes shorter. Although the pressure of the drying chamber after vacuation varies depending upon the size of the sprayed liquid droplets, etc. whereby it is not generally definitive, it is made, for example, into the pressure of about a low vacuum region or, to be more specific, from about 1.0×10^3 to 7.0×10^3 Pa.

In case a spray-drying device having a four-passage nozzle is used, there are two liquid passages in a nozzle as mentioned above and, therefore, when two different microorganism cell liquids or a microorganism cell liquid and

another solution or suspension are sprayed from different liquid passages at the same time, it is possible to manufacture a dried microorganism cell product wherein they are mixed. For example, when microorganism liquids of two different kinds of microorganisms are sprayed at the same time, a dried microorganism cell product containing the said two kinds of microorganisms is obtained. When a microorganism cell liquid and an edible composition are sprayed at the same time, a dried microorganism cell product containing the microorganism cells and the edible composition is obtained.

Examples of the edible composition used in the present invention are a liquid composition of milk, meat, fish, fruit or vegetable. Two or more kinds of them may be mixed therein.

It is preferred that such an edible composition is concentrated to a water content of less than about 70% by weight before the spray-drying where water remained to an extent that the fluidity is not lost.

Examples of the above-mentioned liquid composition of fruit or vegetable are a solution or a suspension where seed, root, tuber, stem, leaf, flower or fruit which is finely ground with or without heating is dissolved or suspended in an appropriate solvent.

Preferred examples of fruit or vegetable are leaves of leek, Welsh onion, asparagus, fennel, cabbage, etc.; stems of rhubarb, broccoli, etc.; seeds of cocoa, pea, soybean or cereals; roots of carrot, onion, *hatsukadaikon* (a kind of Japanese radish), celery, beet, etc.; tubers of casaba, potato, etc.; fruit such as tomato, courgette, eggplant, banana, apple, apricot, melon, watermelon, pear, plum, peach, cherry, kiwi,

sea buckthorn berry, medlar, mirabelle cherry, etc.; and mushroom; etc.

Examples of a liquid composition of milk, meat or fish are a solution or a suspension where milk, egg or meat or fish which is finely ground with or without heating is dissolved or suspended in an appropriate solvent; protein obtained therefrom or its hydrolyzed protein; etc.

In a spray-drying device having a four-passage nozzle, when a microorganism cell liquid is sprayed from one liquid passage while a liquid coating agent of masking agent is sprayed from another liquid passage in the two liquid passages of the nozzle, the microorganism cells can be coated or masked whereupon a coated or masked dry microorganism cell product according to the present invention can be prepared.

As a result of coating of the microorganism cells, it is possible to adjust the time for disintegration or to adjust so as to act in specific organs such as intestine. It is also possible to attempt an improvement of appearance or enhancement of quality. Further, in the case of the pharmaceutical or food containing two or more ingredients and when denaturation takes place by contacting the said ingredients, it is now possible to suppress the denaturation by coating one of or both ingredients.

It is furthermore possible to suppress bitter taste or acidic taste by masking the microorganism cells. Especially, pharmaceutical or food containing high concentrations of lactic acid bacteria or the like has a unique taste and there is an advantage that, when all or a part of the surface of the microorganism cells is coated or masked, such a unique taste

can be reduced.

With regard to the coating agent used in the present invention, there may be used known materials having a coating ability such as hydroxypropyl cellulose (hereinafter, abbreviated as HPC), starch paste, silicone, solution of sugar such as starch syrup or various coating materials.

Examples of the material for enteric coating are hydroxypropyl methylcellulose phthalate (HPMCP), hydroxypropyl methylcellulose acetate succinate (HPMCAS), cellulose acetate phthalate (CAP), carboxymethyl ethylcellulose (CMEC), methacrylic acid-ethyl acrylate copolymer and methacrylic acid-methyl methacrylate copolymer. Examples of other coating material are ethylcellulose, hydroxypropyl methylcellulose, cellulose acetate phthalate and polyvinylacetal diethylaminoacetate.

Examples of the masking agent used in the present invention are aminoacryl methacrylate copolymer E, aminoacryl methacrylate copolymer RS, methacrylic acid copolymer LD and HPC.

When such a coating agent or a masking agent is liquid, the said agent may be used as it is. Alternatively, it may be diluted with a diluent such as water. When the said agent is solid, it is dissolved or suspended in a solvent such as water and is used.

It is also possible that, in place of a coating agent or a masking agent, a wall membrane substance is sprayed from a liquid passage of the four-passage nozzle whereupon microcapsules can be formed.

In that case, it is recommended that the microorganism

cell liquid is prepared by suspending the microorganism in a solvent such as glycerol, medium-chain triglyceride or corn oil which is inert to the microorganism. This is because, when the solvent for the microorganism cells is water, survival rate of the microorganism cells lowers due to the products as a result of a brisk metabolism of the microorganism.

Examples of the wall membrane substance are a cellulose substance such as ethylcellulose; a high-molecular substance such as polylactic acid, polystyrene, polybutadiene and styrene-methyl acrylate copolymer; and hydrogenated oil having a melting point of not lower than body temperature such as hydrogenated palm oil.

When such a wall membrane substance is liquid, the said substance may be used as it is. Alternatively, it may be diluted with a diluent such as water. When the said substance is solid, it is dissolved or suspended in a solvent such as water and is used.

With regard to a method for the manufacture of a dried microorganism cell product which is coated or masked according to the present invention or a method for the manufacture of microcapsules containing the dried microorganism cell product, there may be exemplified not only the above-mentioned method but also a method where the above-mentioned microorganism cell liquid is previously mixed with a coating agent, a masking agent or a wall membrane substance and the resulting mixed liquid is subjected to spray-drying according to the present invention.

With regard to the dried microorganism cell product obtained by the above-mentioned spray-drying according to the present invention, it is possible to prepare a dried

microorganism cell product having a desired particle size by adjusting the gas amount of the compressed gas and the liquid amount of the microorganism cell liquid sent to the nozzle upon checking whether the microorganism cell liquid is a solution or a suspension or checking its concentration and property such as viscosity.

As mentioned already however, it is preferred that the particle size of the dried microorganism cell product is about 1-10 μm by rounding the first decimal factor. This is because, when the particle size is small, static electricity is hardly generated during the step of preparation or pressure to the microorganism cells upon tabletting is small. Incidentally, particle size of the dried microorganism cell product can be easily measured under a microscope.

In order to make the particle size of the resulting dried microorganism cell product small, it is also possible that a treatment which is known *per se* is carried out before the spray-drying. Examples of the known treatment are a treatment where viscosity and surface tension of the microorganism cell liquid are made small and a treatment where the primary particle size is made small or suspending is well conducted when the microorganism cell liquid is a suspension of microorganism cells.

When the particle size of the dried microorganism cell product is made small as mentioned above, there is another advantage that viable cell ratio rises and pharmaceutical or food containing many viable cell count can be provided. Thus, in obtaining a dried microorganism cell product of a single micron size, it is preferred that the sprayed liquid droplets

are in a single micron size. When particle size of the sprayed liquid droplets is small, surface area per unit weight of the sprayed liquid droplets becomes large whereupon contact with drying wind takes place efficiently and, even when temperature of the drying wind is relatively low, an efficient drying is possible whereby extinction or damage of the microorganism cells by heat of the drying wind can be suppressed as much as possible. As a result, viable cell ratio rises to give a dried microorganism cell product having many viable cells.

Therefore, in accordance with the spray-drying of the present invention, it is possible to prepare a dried microorganism cell product where the viable cell count is from about 1.0×10^5 to about 2.0×10^{12} CFU/g, preferably from about 1.0×10^{11} to about 2.0×10^{12} CFU/g, more preferably from about 1.2×10^{11} to about 1.5×10^{12} CFU/g and, most preferably, from about 1.5×10^{11} to about 8.0×10^{11} CFU/g. Measurement of viable cell count in the dried microorganism cell product varies depending upon the microorganism and, for example, it can be easily measured by a quantitative determination method for each microorganism mentioned in the "Japanese Pharmaceutical Codex".

In the present invention, it is also possible to combine the above-mentioned spray-drying with a fluidized layer granulation. Thus, it is possible that a device which is characterized that a step where a fluidized layer granulation is carried out using a powder and a binder and a step where a dried microorganism cell product in a single micron size is prepared by spray-drying are carried out in the same container is used and, in the said device, granulation, spray-drying of

microorganism cells and mixing are continuously carried out.

Up to now, steps of spray-drying, granulation and mixing have been carried out in different devices for each but, when granulation, spray-drying of microorganism cells and mixing are carried out in the same device as such, there are advantages that the manufacturing steps are simplified and, at the same time, homogeneity of a mixture of dried microorganism cell product and granules is improved and classification hardly takes place.

An embodiment of the said device according to the present invention is a device where there are installed a nozzle for spraying the binder by which a binder can be sprayed from the upside to the downside of the drying chamber and a nozzle for spraying of microorganism cell liquid from the upside to the downside of the drying chamber and there is also installed a fluidized layer at the bottom of the device by which the powder can be kept in a fluidized state when the air in the device is sucked by an exhaust fan. Here, the air comprising the fluidized layer may be that which is dried by a dehumidifier known *per se*.

In the said device, it is possible that two spraying nozzles are installed therein and each of them is used as a nozzle for spraying the binder and a nozzle for spraying the microorganism cell liquid and it is also possible that only one spraying nozzle is installed therein and the said spraying nozzle is used as a nozzle for spraying the binder and also as a nozzle for spraying the microorganism cell liquid.

As hereunder, there will be mentioned a specific embodiment of a method for the manufacture of a microorganism

cell composition, characterized in that, a step where a fluidized layer granulation using a powder and a binder and a drying step where a dried microorganism cell product of a single micron size is obtained by spray-drying are carried out using the above-mentioned device. In the following embodiment, a step of a fluidized layer granulation is firstly conducted and then a drying step is conducted although those steps may be done at the same time.

Firstly, a fluidized layer granulation is carried out using a powder and a binder. To be specific, powder is aggregated either by (a) blowing compressed gas, preferably inert gas such as nitrogen gas or carbon dioxide gas, therein from the bottom of the device or by (b) sucking the air in the device using an exhaust fan whereby the binder is sprayed by a nozzle for spraying the binder while the powder is kept in a flowing state so that liquid droplets of the binder are contacted with the fluidized powder.

With regard to a nozzle for spraying the binder, that which is known *per se* may be used although it is preferred to use the above-mentioned four-passage nozzle. When a four-passage nozzle is used, sprayed liquid droplets of the binder become smaller whereby particle size of the granules becomes smaller as well. As a result, time required for drying of the granules becomes shorter making the manufacture efficient. Further, when a four-passage nozzle is used, it is possible to prepare the granules having a relatively uniform particle size. As a result, the steps of grinding and particle size selection can be omitted and, in addition, classification hardly takes place upon mixing of the dried microorganism cell product with the

granules.

Incidentally, particle size of the granules is preferably about 100-500 μm.

After that, a microorganism cell liquid is sprayed from a nozzle for spraying the microorganism cell liquid to prepare a dried microorganism cell product of a single micron size. At that time, in succession to the above stage, compressed gas which is blown thereinto from the bottom of the device or gas in the device sucked by an exhaust fan (hereinafter, they will be generally called "gas for fluidization") also acts as drying wind and dries the sprayed liquid droplets of the microorganism cell liquid and, at the same time, it also conducts the mixing with the granules which are in a fluidized state by the gas for fluidization.

Not only the case where particles of the granules and particles of the dried microorganism cell product are independent each other and are mixed together but also the case where particles of the power and particles of the dried microorganism cell product form one particle by a binder and also the case where the said particle and particles of granules and/or particles of the dried microorganism cell product are mixed are exemplified as the mode of the resulting mixture. A microorganism cell composition which is characterized in that a dried microorganism cell product of a single micron size is adhered to granules comprising powder and binder as such can be easily manufactured.

With regard to a nozzle for spraying the binder, that which is known *per se* may be used although it is preferred to use the above-mentioned four-passage nozzle. This is because, when a

four-passage nozzle is used, the advantage of the four-passage nozzle in the case of the above-mentioned spray-drying is able to be achieved in this manufacturing method as well.

The above-mentioned device and an embodiment of the method for the manufacture of a microorganism cell composition in accordance with the present invention will be illustrated by referring to Fig. 4.

With regard to the fluidized layer granulation, under the state where powder 48 is placed in the main body of the device 41 according to the present invention equipped with a fluidized bed 42, an exhaust fan is driven together with spraying of a binder 45 from a nozzle for spraying the binder 47 and gas for fluidization 49 heated by a heat exchanger is continuously introduced from the side of the lower part of the main body of the device 41. At that time, the gas for fluidization 49 may be previously dried using a dehumidifier (not shown). The introduced gas for fluidization 49 is sucked upward by an exhausting fan. When velocity of the gas for fluidization 49 becomes high, the powder 48 is blown up from the fluidized bed 42 and floated/suspended in the air whereupon the so-called fluidized layer is formed. The liquid droplets of the binder 45 are contacted with the said fluidized powder 48 to aggregate the powder 48 whereby granulation can be carried out.

With regard to spray-drying, when a microorganism cell liquid 44 is sprayed using a nozzle 46 for spraying the microorganism cell liquid, sprayed liquid droplets of the said microorganism cell liquid are dried by the gas for fluidization 49 which is pulled upward from the fluidized bed 42 by an exhausting fan. At that time, it is appropriate to lower, if

desired, the temperature of the gas for fluidization 49 than that in the case of fluidizing granulation to an extent of about 2-400°C, preferably about 5-250°C, more preferably about 5-150°C or, still more preferably, about 20-70°C. This is because extinction or damage of the microorganism cells by heating of the gas for fluidization is suppressed as much as possible.

The granules and the dried microorganism cell product manufactured as such are mixed by a gas for fluidization 49 in the device 41.

Although there is no particular limitation for the above powder used for the fluidized layer granulation, that which is able to be administered or taken together with the dried microorganism cell product.

Specific examples thereof are a substance having a pharmacological action other than the dried microorganism cell product, an excipient and other finely-powdered food material. With regard thereto, that which has been known *per se* may be used or a mixture of two or more thereof may be used.

Examples of the said finely-powdered food material are spices such as dried and ground spices and herbs (e.g., cinnamon, ginger, mustard, nutmeg, pepper, saffron, sesame, turmeric, parsley, mint, celery, onion and garlic) and other spices prepared by mixing the above spices and herbs such as curry powder and mixed spice; powdery juice of fruit such as apple, orange, lemon, strawberry, pineapple, grapefruit, grape, melon and lime; powdery beverage such as coffee, green tea, English tea, oolong tea, cocoa and barley tea; powered extract of animal such as beef extract, pork extract, chicken extract, scallop extract, *asari* (short-necked clam) extract, oyster extract,

crab extract, shrimp extract and dried bonito extract; powdered extract of plants such as garlic extract, onion extract, celery extract, cabbage extract and trefoil extract; powdery milk product such as skim milk, powdered milk containing fat and fermented milk powder; egg yolk powder and total egg powder; and cereal powder, hydrolyzed protein of animals and plants, table salt, amino acids and seasoning powder of a nucleic acid type.

The binder for the fluidized layer granulation is an additive which enhances the binding force among the particles of the powder or between the dried microorganism cell product and the particles of the powder, and its representative example is a water-soluble high-molecular substance. To be more specific, there may be exemplified hydroxypropyl cellulose, hydroxypropyl methylcellulose and methylcellulose. Besides the above, it is also possible to use polyvinylpyrrolidone, gelatin, polyvinyl alcohol, starch paste liquid or sugar liquid as a binder.

If desired, a compounding agent may be added to the binder. With regard to the compounding agent, that which has been known *per se* may be used and its examples are natural or synthetic surface-active agent such as lecithin, quillaia saponin, sucrose fatty acid ester, glycerol fatty acid ester, polyglycerol fatty acid ester and propylene glycol fatty acid ester; protein such as gelatin, casein, water-soluble peptide, soybean protein, albumin and gluten; etc.

The pharmaceutical or food containing the dried microorganism cell product in accordance with the present invention may contain other ingredients provided that it

contains the dried microorganism cell product in accordance with the present invention.

For example, it may contain ingredients having other pharmacological actions or other foods and, if desired, it may contain additives or filling materials having other desired functions.

The dried microorganism cell product prepared by spray-drying as mentioned above can be made into the pharmaceutical or food containing the dried microorganism cell product of the present invention either as it is in a form of diluted powder or granules or as a form of tablets, pills or troches.

When the pharmaceutical or food containing the dried microorganism cell product of the present invention is in a form of diluted powder or granules, the dried microorganism cell product obtained by the above spray-drying may be used as it is or may be subjected to a treatment known *per se* being carried out in the art.

When the pharmaceutical or food containing the dried microorganism cell product of the present invention is in a form of tablets, it is manufactured by tabletting the dried microorganism cell product obtained by the above spray-drying using a tabletting machine. With regard to the tabletting machine, known ones such as a tabletting machine of a rotary type may be used.

It is also possible that the dried microorganism cell product obtained by the above spray-drying according to the present invention is mixed with an additive which is usually powdery or granular and has been commonly used in the art such

as a excipients, a binder, a disintegrating agent or an antistatic agent in a usual compounding ratio and the resulting mixture is tabletted by a tabletting machine.

It is further possible that the resulting tablets are subjected to coating or masking such as sugar coating, enteric coating or film coating. With regard to a coating agent or a masking agent, known ones such as the above-mentioned ones may be used. Incidentally, coating or masking may be carried out by a known method or a method similar thereto.

The above-mentioned tablets may be sustained-released tablets. Examples of the sustained-released tablets are gradumet where the dried microorganism cell product obtained by the above spray-drying is dispersed in a plastic lattice which is discharged outside the body as it is; wax matrix where the dried microorganism cell product obtained by the above spray-drying is dispersed in a wax lattice in a spongy shape; resinate where the dried microorganism cell product obtained by the above spray-drying is adsorbed with ion-exchange resin; and spantab comprising a plurality of layers where dissolving and releasing properties are different. Those sustained-released tablets may be manufactured by a known method or by a method similar thereto.

When the pharmaceutical or food containing the dried microorganism cell product of the present invention is in a form of pills or troches, they may be manufactured by the same manner as in the case of tablets. In the case of troches however, no disintegrating agent is usually added since they are gradually dissolved or disintegrated in the mouth.

The dried microorganism cell product obtained by the

above spray-drying may be filled in capsules to prepare a capsule preparation. With regard to a capsule material, known capsule materials such as gelatin may be used. In the case of a soft capsule preparation, there may be used a plasticizer such as glycerol or sorbitol. It is also possible that the dried microorganism cell product obtained by the above spray-drying is subjected to a compressive molding by means of tabletting for example and the molded one is impregnated in fat/oil or the like if necessary, then coated with solid fat/oil and coated with a capsule material. As a result thereof, water does not directly contact with the dried microorganism cell product even when water is permeated inside through the capsule coat whereby damage or extinction of the microorganism cells by water can be prevented.

It is also possible that microcapsule is prepared using polylactic acid or the like according to the conventionally known method.

The pharmaceutical or food containing the dried microorganism cell product according to the present invention may be in a liquid form such as pharmaceutically acceptable solution, suspension, syrup or elixir.

Examples of the diluent used are pure water, vegetable oil and ethanol. Besides the diluent, it is also possible to mix with an additive such as moisturizer, suspending agent, sweetener, flavor, aromatizer and antiseptic.

It is preferred to prepare the suspension in such a manner that the dried microorganism cell product prepared by the above spray-drying is added to a solvent such as water or vegetable oil together with a suspending agent or other desired additive

and suspended by a known method so as to make the mixture homogeneous. With regard to the suspending agent, known ones such as gum arabic, carmellose sodium, methylcellulose and sodium alginate may be used.

It is preferred to prepare the syrup preparation in such a manner that the dried microorganism cell product prepared by the above spray-drying is dissolved or suspended in a diluent such as pure water together with sucrose and, if desired, with other saccharide or sweetener. It is also possible to prepare a dry syrup preparation which is used by dissolving or suspending the dried microorganism cell product upon actual use.

It is preferred to prepare the elixir preparation in such a manner that the dried microorganism cell product prepared by the above spray-drying is dissolved in sweet and aromatic ethanol together, if desired, with additives. The amount of ethanol is preferably about 4-40% by weight.

It is also possible that the pharmaceutical containing the dried microorganism cell product of the present invention is made into parenteral injection preparations such as aqueous injection, non-aqueous injection, aqueous suspension injection or non-aqueous suspension injection.

It is preferred to prepare the injection preparation in such a manner that the dried microorganism cell product prepared by the above spray-drying is dissolved in a solvent together, if desired, with additives followed by filtering or is suspended in a solvent and then charged in a container, the container is tightly sealed and sterilization is carried out.

Examples of the solvent are aqueous solvent such as

distilled water for injection, physiological saline and Ringer's solution; and non-aqueous solvent such as propylene glycol, polyethylene glycol, vegetable oil such as olive oil and alcohol such as ethanol.

Examples of the additive are (a) stabilizer such as ethylenediamine; (b) preservative such as p-hydroxybenzoate, benzyl alcohol, chlorobutanol, phenol and cresol; (c) surface-active agent such as polyoxyethylene hydrogenated castor oil and sucrose fatty acid ester or solubilizer such as lecithin and hydrogenated lecithin; (d) isotonizing agent such as sodium chloride, glucose and glycerol; (e) buffer such as phosphate and citrate; and (f) suspending agent such as gum arabic, carmellose sodium, methylcellulose and sodium alginate.

The pharmaceutical or food containing the dried microorganism cell product according to the present invention may also be used for promoting the healthy state of mammals. It may be also used as agricultural chemical or as additive for feed.

For example, lactic acid bacteria have been known as one of the useful enteric bacteria and have been said to be deeply participated in health. Particularly with regard to physiological significance of bifidobacteria, lactococci and lactobacillus, there have been many reports whereby their action of suppressing the malignant microorganisms by production of organic acid such as lactic acid or acetic acid in the intestine, their production of vitamins, their immunological enhancement, etc. have been made clear. Accordingly, there have been developed many products such as

pharmaceuticals or foods containing lactic acid bacteria with an object of maintenance and enhancement of health and prevention or therapy of diseases of human being, livestock or pet animals.

In addition, lactic acid bacteria have been said to have deeply participated in the improvement of taste and preservation or to the maintenance of quality during the manufacturing steps of food such as soybean paste, soybean sauce, pickles and *sake* (Japanese rice wine) and have been utilized therefor.

The pharmaceutical containing lactic acid bacteria or bifidobacteria according to the present invention is able to be used for the therapy or prevention of diarrhea, constipation, hypercholesterolemia, hepatic disease, immunosuppressed disease, enteritis (such as gastroenteritis or colitis), etc.; recovery of intestine after disorder by food, pharmaceutical, chemical or physical pharmaceutical or after surgical invasion, chemotherapy or contagious disease; and for the inhibition of absorption of endotoxin and also for the antagonism against the formation of endogenous toxin.

This is because the said pharmaceutical has an action of recovering the intestinal mucous membrane and also adjusting the enzyme potential of intestinal tract when it changes as a result of the state of stress. This is also because it has an action of normalizing the function of intestinal flora, promoting the synthetic, digestive or enzymatic and absorptive steps of vitamins and proteins, preventing the formation of colonies of pathogenic microorganisms and stimulating the immunoreaction.

An example of the use of the food containing the dried microorganism cell product of lactic acid bacteria or bifidobacteria according to the present invention is that the dried microorganism cell product prepared by the above spray-drying is added to milk product such as yogurt or cheese, confectionery or beverage.

It is also possible that the dried microorganism cell product prepared by the above spray-drying *per se* is used as a seasoning. It is further possible that the dried microorganism cell product prepared by the above spray-drying is dissolved or suspended in a solvent such as water or oil and is used as a seasoning. It is furthermore possible that it is mixed with other seasonings.

The dried microorganism cell product of lactic acid bacteria prepared by the above spray-drying is able to be used as a starter for a stable production of food by lactic acid fermentation on an industrial scale.

Powdery lactic acid bacteria starter may be used, for example, for milk products, rye bread and fermented sausage.

The dried microorganism cell product of yeast prepared by the above spray-drying is able to be used in wine industries such as beer, *sake* (Japanese rice wine) and wine utilizing the property that yeast briskly carries out alcohol fermentation. It is also able to be used for fermentation of bread or the like.

Further, since yeast extract which is an autolyzed liquid or extract with hot water of yeast contains a lot of vitamins, organic bases or amino acids and is of a high nutritive value, the dried microorganism cell product of yeast extract prepared by the above spray-drying is able to be used as pharmaceutical

such as a vitamin preparation and as a health food.

The dried microorganism cell product of koji mold prepared by the above spray-drying is able to be used for the manufacture of *sake* (Japanese rice wine), *amazake* (a sweet drink made from fermented rice), *shochu* (Japanese distilled spirits), soybean paste, *mirin* (sweet *sake* for seasoning) or soybean sauce. There are many cases where *Aspergillus oryzae* is used although, for the manufacture of alcohol, *Asp. niger* may be sometimes used instead.

In addition, many of koji mold strains produce various kinds of enzymes such as amylase and protease, various kinds of organic bases, vitamins, etc. and, therefore, the dried microorganism cell product of koji mold prepared by the above spray-drying in accordance with the present invention is able to be used as pharmaceutical such as a digestive enzyme preparation and a vitamin preparation or as health food.

Example 1

(Incubation of microorganism cells)

Incubated liquid of *Bifidobacterium bifidum* which was previously grown in a GAM medium (manufactured by Nissui Seiyaku K. K.) was inoculated in 0.1% by weight to the same medium and then incubated at 37°C for 16 hours. This was centrifuged and the resulting precipitate was used as wet microorganism cells.

(Preparation of microorganism suspension)

To an aqueous solution of 0.5M of mannitol, 0.5M of sodium glutamate, 0.1M of arginine, 0.1M of sodium succinate and 0.01M of magnesium sulfate was added dextrin to make 35% by weight and in this dispersing medium prepared as such were suspended

the above-prepared wet microorganism cells.

(Measurement of viable cell count in the suspension of the microorganism)

Measurement was carried out by a quantitative determination method for bifidobacteria mentioned under the item of " Bifidobacteria" in the "Japanese Pharmaceutical Codex". Thus, 1 mL of the microorganism suspension was taken and diluted using a diluent prepared as mentioned below by a ten-fold dilution method so as to make the viable cell count 20-200 per mL. This liquid (1 mL) was placed on a Petri dish and 20 mL of agar medium for the test of bifidobacteria kept at 50°C were added thereto followed by quickly mixing to solidify. This was subjected to an anaerobic culture at 37°C for 60 hours and viable cell count in the microorganism suspension was determined from the appeared colony numbers and the diluting ratio.

The agar medium for the test of bifidobacteria was prepared in such a manner that, among the following components, those except equine blood were dissolved by heating, adjusted to pH 7.2, sterilized by heating at 115°C for 20 minutes using a high-pressure steam sterilizer and cooled down to 50°C and equine blood was added thereto.

Percolate of bovine liver	150 mL
Peptone prepared from meat	10 g
Peptone made of casein	5 g
Yeast extract	5 g
Meat extract	3 g
Peptone made of soybean	3 g
Glucose	10 g

Potassium monohydrogen phosphate	1 g
Potassium dihydrogen phosphate	1 g
Starch	0.5 g
L-Cysteine hydrochloride	0.5 g
Magnesium chloride	0.2 g
Sodium chloride	0.01 g
Ferrous sulfate	0.01 g
Manganese sulfate	7 mg
Polysolvate 80	1 g
Agar	15 g
Equine blood	50 mL
Pure water	790 mL

pH: 7.1-7.3

The above-mentioned diluent was prepared in such a manner that the following components were mixed and sterilized by heating at 121°C for 15 minutes using a high-pressure steam sterilizer.

Anhydrous sodium monohydrogen phosphate	6.0 g
Potassium dihydrogen phosphate	4.5 g
Polysolvate 80	0.5 g
L-Cysteine hydrochloride	0.5 g
Agar	1.0 g
Pure water	1000 mL

pH: 6.8-7.2

(Spray-drying)

The microorganism suspension prepared as mentioned above was spray-dried by a spray-drying machine as shown in Fig. 2 where a four-passage nozzle (as mentioned in the Japanese Patent No. 2,797,080) was integrated. Thus, the microorganism

suspension was supplied from the two liquid passages at the rate of 8 mL/minute (4 mL/minute/1 mm nozzle) while compressed gas was supplied from the two gas passages at the rate of 40 NL/minute (converted value at 20°C) and the resulting sprayed liquid droplets were dried by drying wind to prepare the dried microorganism cell product of the present invention. Incidentally, the drying wind was supplied at the inlet temperature of 100°C and at the rate of 1.0 m^3/minute into the drying chamber and its outlet temperature was 67°C.

(Measurement of viable cell count in the dried microorganism cell product)

Viable cell count in the resulting dried microorganism cell product was measured according to a quantitative determination method for bifidobacteria mentioned under the item of "Bifidobacteria" in the "Japanese Pharmaceutical Codex". Thus, 5 g of the dried microorganism cell product were taken to the same diluent mentioned above which was previously warmed at 37°C whereupon the total volume was made 50 mL. This was well stirred and then warmed at 37°C for 30 minutes to prepare an original sample solution. This was diluted with a diluent liquid by a 10-fold dilution method so as to make the viable cell count 20-200 in 1 mL. This liquid (1 mL) was placed on a Petri dish and 20 mL of agar medium for the test of bifidobacteria kept at 50°C were added thereto followed by quickly mixing to solidify. This was subjected to an anaerobic culture at 37°C for 60 hours and viable cell count in the microorganism suspension was determined from the appeared colony numbers and the diluting ratio.

The same experiments were further carried out where the

inlet temperature of the drying wind was made 80°C, 50°C and 50°C successively.

Comparative Example 1

The microorganism suspension prepared by the same manner as in the Example was freeze-dried. The freeze-drying condition was that the shelf temperature was 30°C or lower and the final degree of vacuum was 0.1 Torr (13.3 Pa).

Viable cell count in the powder after drying was measured by the same manner as in Example 1.

Viable cell count and survival rate in the Example and the Comparative Example are shown in Table 1.

Here, the survival rate was calculated by the following formula.

Survival rate (%) = {((Viable cell count per gram of dried microorganism cell product) × (Solid content of the microorganism suspension))/(Viable cell count per gram of dried microorganism cell product)} × 100

Table 1

	Inlet Temp (°C)	Exhaust Temp (°C)	Viable Cell Count in Powder (CFU/g)	Survival Rate (%)	Comparison with Comp. Ex. (%)
Example	100	67	1.65×10^{11}	52	104
	80	56	1.80×10^{11}	55	113
	60	44	2.28×10^{11}	72	143
	50	37	2.43×10^{11}	77	153
Comp. Ex.			1.59×10^{11}	50	100

(Note: Comp. Ex. means Comparative Example)

As shown in Table 1, it has been found that, when the spray-drying in accordance with the present invention is carried out, dried microorganism cell products having a higher survival rate than that by freeze-drying are able to be prepared.

(Particle size of dried microorganism cell product)

The dried microorganism cell product of the present invention prepared by making the inlet temperature 60°C in Example 1 was measured under a microscope (Digital HD Microscope VH-7000 manufactured by Keyence Corp.). Distribution of the particle size was as follows.

Table 2

Particle Size	Ratio (%)
1-5 μm	39
5-10 μm	31
10-20 μm	26
20-50 μm	4

Example 2

As same as in Example 1, microorganism cells were incubated, the microorganism suspension was prepared and viable cell count in the microorganism suspension was measured.

(Spray-granulation)

There was used a device where, in the fluidized layer granulator FLO-120 (manufactured by Freund Inc.), four-passage nozzle (that mentioned in the Japanese Patent No. 2,797,080) was integrated in the conventional two-passage spraying nozzle

and then a lactic acid bacteria suspension was sprayed into the fluidized layer to prepare the powder containing the lactic acid bacteria.

The steps were roughly classified into two and, in the first step, a binder was blown upon an excipient as granulates using the two-passage nozzle to conduct the granulation. In the second step, a lactic acid bacteria suspension was spray-dried using the four-passage nozzle in the same state that the fluidized layer was kept at low temperature and, at that same time, it was mixed with the granulates obtained in the first step.

The operating condition of the machine used in this experiment was that the amount of supplied air was 70 m^3/minute and the amount of nozzle air was 40 NL/minute (value converted at 20°C).

Compositions of the excipient and the binder used for the granulation were as follows.

Excipient:	Corn starch	40 kg
	Crystalline cellulose	40 kg
	Lactose	40 kg
Binder:	Corn starch	1.8 kg
	Pure water	60 L

The first step will be illustrated in detail as follows. The above-mentioned excipient materials (120 kg) was weighed and placed in a hopper, temperature of supplying air was set at 100°C, dry air was sent therein to form a fluidized layer and the binder was sprayed using a two-passage nozzle at the liquid flow rate of 1.6 L/minute. The exhaust gas temperature at that time was 45-50°C and the temperature in the fluidized

layer was 55-60°C. When spraying of the binder was finished, the fluidized layer was dried as it was for 20 minutes to give granulates containing low amount of water.

The second step will be now illustrated in detail as follows. After completion of the post-drying of the granulates, the microorganism suspension (350 L) prepared by the same manner as in Example 1 was sprayed at the liquid flow rate of 16 mL/minute using the four-passage nozzle under the state where the temperature of supplying air was lowered to 70°C. At that time, the exhaust gas temperature was 30-35°C and the temperature in the fluidized layer was 35-40°C. As a result of spray-drying at such a low temperature, lactic acid bacteria were pulverized and, when they were mixed in the fluidized layer at the same time, powder containing the lactic acid bacteria according to the present invention was obtained.

Comparative Example 2

There was prepared a mixed powder of lactic acid bacteria where an adjustment was done so as to contain the same amount of the lactic acid bacteria in the preparation.

The microorganism cell powder (2 g) prepared in Example 1 was diluted to an extent of ten-fold using corn starch to make 20 g, added to 1180 g of the granulates comprising the excipient and the binder prepared in the first step of Example 2 and mixed at 100 rpm for 3 minutes using a mixer of type V to prepare a mixed lactic acid bacteria powder.

Viable cell count contained in 1 g of the powder obtained in Example 2 or Comparative Example 2 was measured according to the item of (Measurement of viable cell count in the dried microorganism cell product) of Example 1. In Example 2, the

viable cell count was 5.12×10^8 (CFU/g) and, in Comparative Example 2, it was 4.85×10^8 (CFU/g).

It has been therefore found that, in accordance with the present invention where spray-drying and fluidized layer granulation are combined, it is possible to simplify the manufacturing steps in which at least the same or even more viable cell rate can be still maintained as in the case of the conventional manufacturing method for the powder comprising spray-drying, granulation and mixing steps.

Example 3

To 500 g of distilled water, the following components were added followed by stirring to prepare a coating agent.

Composition of the coating agent:

Eudragit® L30D-55	500 g
Polyethylene glycol 6000	15 g
Tween® 80	7.5 g
Talc	45 g

In the meanwhile, a microorganism suspension was prepared by the same manner as in Example 1.

Spray-drying was carried out using a spray-drier as shown in Fig. 2 where a four-passage nozzle (as mentioned in the Japanese Patent No. 2,797,080) was integrated. Thus, a microorganism suspension was supplied at the rate of 5 g/minute from one liquid passage in the four-passage nozzle comprising two liquid passages and two gas passages, a liquid coating agent was supplied at the rate of 20 g/minute from another liquid passage and compressed gas was supplied at the rate of 40 NL/minutes from the two liquid passages and the resulting spray-dried liquid droplets were dried by drying wind to

manufacture a dried microorganism cell product which was partially coated according to the present invention.

Incidentally, inlet temperature of the drying wind was 100°C and the wind was supplied at the rate of 1.0 m^3/minute into a drying chamber of 0.9 mPa.

Each 10 mg of the conventional bifidobacterial powder and the partially-coated dried microorganism cell product according to this Example were taken and subjected to a palatability test whereupon the taste of the partially-coated dried microorganism cell product according to this Example was improved.

Example 4

The microorganism suspension (100 g) prepared in the same manner as in Example 1 and an enteric coating material having the following composition were mixed and the said mixture was spray-dried using a spray-drier as shown in Fig. 2 where a four-passage nozzle (as mentioned in the Japanese Patent No. 2,797,080) was integrated. Thus, a mixed solution was supplied from the two liquid passages at the rate of 5.6 g/minute while compressed gas was supplied from the two gas passages at the rate of 40 NL/minute and the resulting spray-dried droplets were dried by drying wind to manufacture an enteric-coated dried microorganism cell product according to the present invention.

Incidentally, inlet temperature of the drying wind was 80°C and it was supplied at the rate of 1.0 m^3/minute into a drying chamber of 0.9 mPa.

Enteric coating material:

AQOAT (manufactured by Shin-Etsu Chemical)

30 g

Triethyl citrate	8.4 g
Distilled water	161.6 g

(Acid resistance test of the enteric-coated dried microorganism cell product)

An acid resistance test was carried out using the first liquid (pH 1.2; 36-38°C) mentioned in "General Test Method - Disintegration Test Method" of the Japanese Pharmacopoeia. The first liquid was placed in a container of about 1000 mL which was able to keep warm and kept at 36-38°C. To this was added a dried microorganism cell product followed by well stirring and each 1 mL was sampled after 5, 15, 30 and 60 minute(s) from the addition of the dried microorganism cell product. The sampled specimen was successively diluted to appropriate concentrations using a diluent mentioned in Example 1 and measurement of viable cell count was carried out as same as in Example 1. Incidentally, the first liquid of the pharmacopoeia was an artificial gastric juice where 2.0 g of sodium chloride are added to and dissolved in 7 mL of hydrochloric acid and distilled water to make 1000 mL.

The same test was carried out for the conventional bifidobacterial powder as well.

Fig. 3 shows the relation between the protected time of the first liquid and the viable cell count. In the conventional microorganism cell powder, viable cell count became 1/1000 or less after 5 minutes from pouring and, after 30 minutes and thereafter, no viable cell was noted while, in the coated microorganism cell powder according to the present invention, about 1% of viable cells were noted even after 60 minutes from pouring. Thus, as a result of conducting the above-mentioned

coating, resistance of the dried microorganism cell product to acid was significantly improved.

Example 5

A microorganism suspension was prepared by the same manner as in Example 1 except that *Lactobacillus acidophilus* was used as the microorganism.

Viable cell count in the microorganism suspension was measured according to quantitative determination of lactomin mentioned under the item of "Lactomin" in the Standards for Pharmaceuticals Unlisted in the Japanese Pharmacopoeia. Thus, 1 mL of the microorganism suspension was taken and diluted with a diluent liquid prepared as mentioned below by a 10-fold dilution method so as to make the viable cell count 20-200 in 1 mL. This liquid (1 mL) was placed on a Petri dish and 20 mL of agar medium for the test of lactomin kept at 50°C were added thereto followed by quickly mixing to solidify. This was incubated at 37°C for 48 hours and viable cell count in the microorganism suspension was determined from the appeared colony numbers and the diluting ratio.

Here, the agar medium for the test of lactomin was prepared in such a manner that the following components were mixed and sterilized by heating at 121°C for 15 minutes using a high-pressure steam sterilizer.

The tomato juice used here was prepared in such a manner that the same amount of pure water was added to tomato juice and the mixture was boiled with occasional stirring, adjusted to pH 6.8 and filtered.

Peptone made of casein	20 g
yeast extract	5 g

Meat extract	15 g
Glucose	20 g
L-Cysteine hydrochloride	1 g
Polysolvate 80	3 g
Tomato juice	200 mL
Agar	20 g
Pure water	800 mL

pH: 6.8

The above diluent liquid was prepared in such a manner that the following components were mixed and sterilized by heating at 121°C for 15 minutes using a high-pressure steam sterilizer.

Sodium monohydrogen phosphate	6.0 g
Potassium dihydrogen phosphate	4.5 g
Polysolvate 80	0.5 g
L-Cysteine hydrochloride	0.5 g
Agar	1.0 g
Pure water	1000 mL

pH: 6.9

The microorganism suspension prepared as above was spray-dried by the same manner as in Example 1.

The operation condition of the machine was as same as in Example 1 except that the inlet temperature was 60°C and the exhaust gas temperature was 45°C.

Viable cell count in the resulting dried microorganism cell product was measured according to quantitative determination of lactomin mentioned under the item of "Lactomin" in the Standards for Pharmaceuticals Unlisted in the Japanese Pharmacopoeia. Thus, 5 g of the dried microorganism

cell product were taken by a diluent liquid which was previously warmed at 37°C to make the total volume 50 mL. This was well stirred and warmed at 37°C for 30 minutes to give an original specimen liquid. This was diluted with a diluent liquid by a 10-fold dilution method so as to make the viable cell count 20-200 in 1 mL. This liquid (1 mL) was placed on a Petri dish and 20 mL of agar medium for the test of lactomin kept at 50°C were added thereto followed by quickly mixing to solidify. This was subjected to an anaerobic culture at 37°C for 48 hours and viable cell count in the microorganism suspension was determined from the appeared colony numbers and the diluting ratio.

The viable cell count in the dried microorganism cell product was 7.24×10^{11} (CFU/g) and the survival rate was 90%. Incidentally, the survival rate was determined by the same manner as in Example 1.

It has been therefore found that, when spray-drying in accordance with the present invention is used, survival rate of the microorganism cells is improved whereby a dried microorganism cell product containing a very high viable cell count is able to be prepared.

Industrial Applicability

As a result of using a spray-drying device equipped with a device for preparing fine particles by which sprayed liquid droplets in a single micron size can be formed, surface area per unit weight of the sprayed liquid droplets becomes bigger and contact with drying wind proceeds very efficiently. Accordingly, when drying is carried out by drying wind of the

temperature which is in the same degree as that in the conventional spray-drying, time required for drying the microorganism cell liquid becomes shorter and extinction or damage of the microorganism cells can be suppressed as much as possible. Further, even when the temperature of drying wind is made lower than the temperature of drying wind in the conventional spray-drying, a sufficient drying is possible without deteriorating the yield or stability and, furthermore, since the temperature of drying wind is low, extinction or damage of the microorganism cells due to heat of drying wind can be suppressed as much as possible. Therefore, in accordance with the method for the manufacture of a dried microorganism cell product in accordance with the present invention, it is now possible to prepare a dried microorganism cell product containing much viable cell count.

Further, in the dried microorganism cell product containing the particles of a single micron size prepared by drying the sprayed liquid droplets having small particle size as such with drying wind, the pressure to be applied to the microorganism cells upon compressive molding, etc. is small and static electricity is hardly generated whereupon they are easily made into pharmaceutical or food in a preparation form such as tablets.

When a spray-drying device equipped with a four-passage nozzle comprising two liquid passages and two gas passages is used as a spray-drying device of the present invention, spraying in large amount is possible and manufacturing efficiency is improved because there are two liquid passages and, in addition, when two different solutions or suspensions are sprayed from

different liquid passages at the same time, it is possible to manufacture a dried microorganism cell product wherein they are mixed.

Further, when a liquid masking agent or coating agent is sprayed from one of the liquid passages while a microorganism cell liquid is sprayed from another liquid passage, it is possible to manufacture a dried microorganism solid product which is masked or coated. Therefore, it is no longer necessary to carry out masking and coating separately whereby the manufacturing steps become simple. Similarly, when a capsule material is sprayed together with a microorganism cell liquid, it is also possible to manufacture microcapsules.

Furthermore, when a spray-drying device having a four-passage nozzle is used, particle size distribution becomes within a relatively narrow range and, accordingly, steps of particle size selection, sieving, etc. thereafter are easily carried out.

Still further, when a device which is characterized in that a step of conducting a fluidized layer granulation using powder and binder and a step of preparing a dried microorganism cell product of a single micron size by spray-drying are carried out in the same container in accordance with the present invention is used and there are continuously carried out granulation, spray-drying of microorganism cells and mixing in the said device, the manufacturing steps can be simplified and, at the same time, homogeneity of mixture of the dried microorganism cell product with the granulates is improved and classification hardly takes place as well.

Claims

1. A method for the manufacture of a dried microorganism cell product having a value of the particle size of 1-10 μm by rounding the first decimal factor wherein viable cell count is from 1.0×10^5 to 2.0×10^{12} CFU per gram, characterized in that, microorganism cell liquid is sprayed to form sprayed liquid droplets having a value of the particle size of 1-10 μm by rounding the first decimal factor and then the sprayed liquid droplets are air-dried by a spray-drying device.

2. The method for the manufacture of the dried microorganism cell product as defined in claim 1, wherein viable cell count is from 1.0×10^{11} to 2.0×10^{12} CFU per gram.

3. The method for the manufacture of the dried microorganism cell product as defined in claim 1 or 2, wherein the microorganism is bifidobacteria, Lactobacillus, lactococci, sporogenous lactic acid bacteria, saccharification bacteria, yeasts, koji molds, actinomycetes, *Bacillus toyoi, B. licheniformis*, butyric acid bacteria, acetic acid bacteria or amino acid fermentation bacteria.

4. The method for the manufacture of the dried microorganism cell product as defined in any one of claims 1 to 3, wherein the microorganism is bifidobacteria.

5. The method for the manufacture of the dried microorganism cell product as defined in any one of claims 1 to 4, wherein the dried microorganism cell product is further coated or masked.

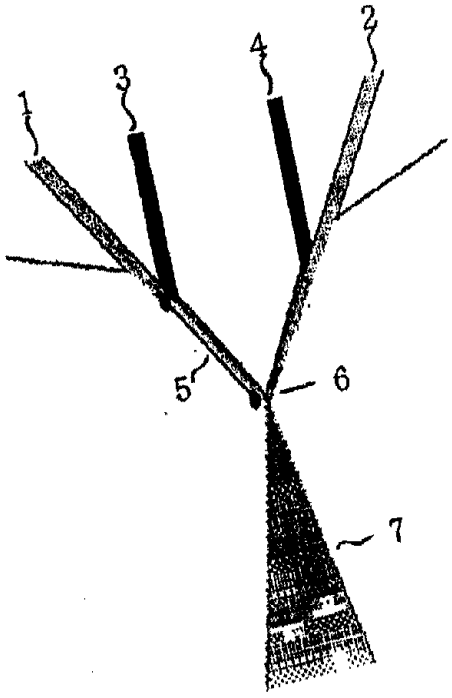
6. The method for the manufacture of the dried microorganism cell product as defined in any one of claims 1 to 5, wherein the sprayed liquid droplets having a value of the particle size of 1-10 μm by rounding the first decimal factor are formed by a four-passage nozzle.

7. The method for the manufacture of the dried microorganism cell product as defined in any one of claims 1 to 6, wherein the temperature of drying air is 5-150°C at an inlet of a drying chamber of the spray-drying device.

8. The method for the manufacture of the dried microorganism cell product as defined in any one of claims 1 to 7, wherein a liquid coating agent or masking agent is sprayed together with the microorganism cell liquid to form sprayed liquid droplets and the said sprayed liquid droplets are air-dried.

9. The method for the manufacture of the dried microorganism cell product as defined in claim 8, wherein the microorganism cell liquid is supplied from one liquid passage in a four-passage nozzle having two liquid passages and two gas passages, a liquid coating agent or masking agent is supplied from another liquid passage, compressed gas is supplied from the two gas passages and the resulting sprayed liquid droplets are air-dried.

Fig.1



IFF000658488

Fig.2

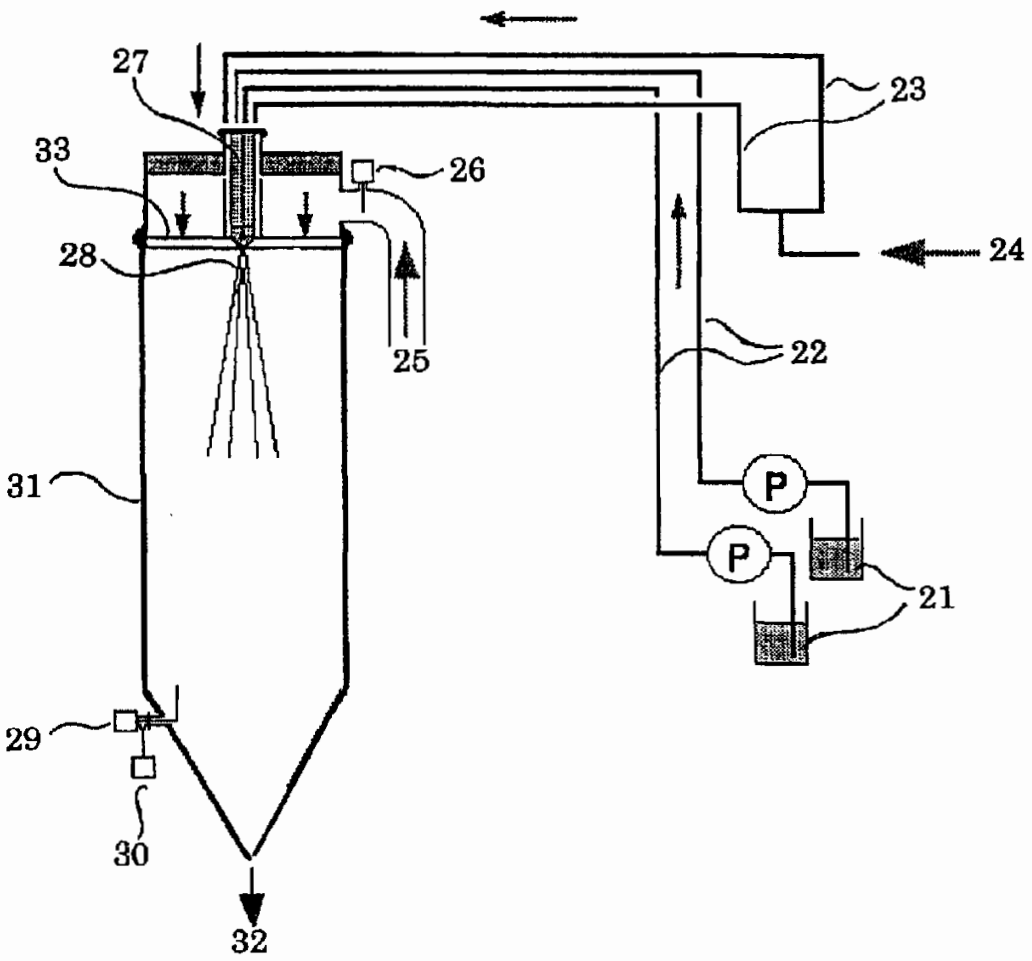


Fig.3

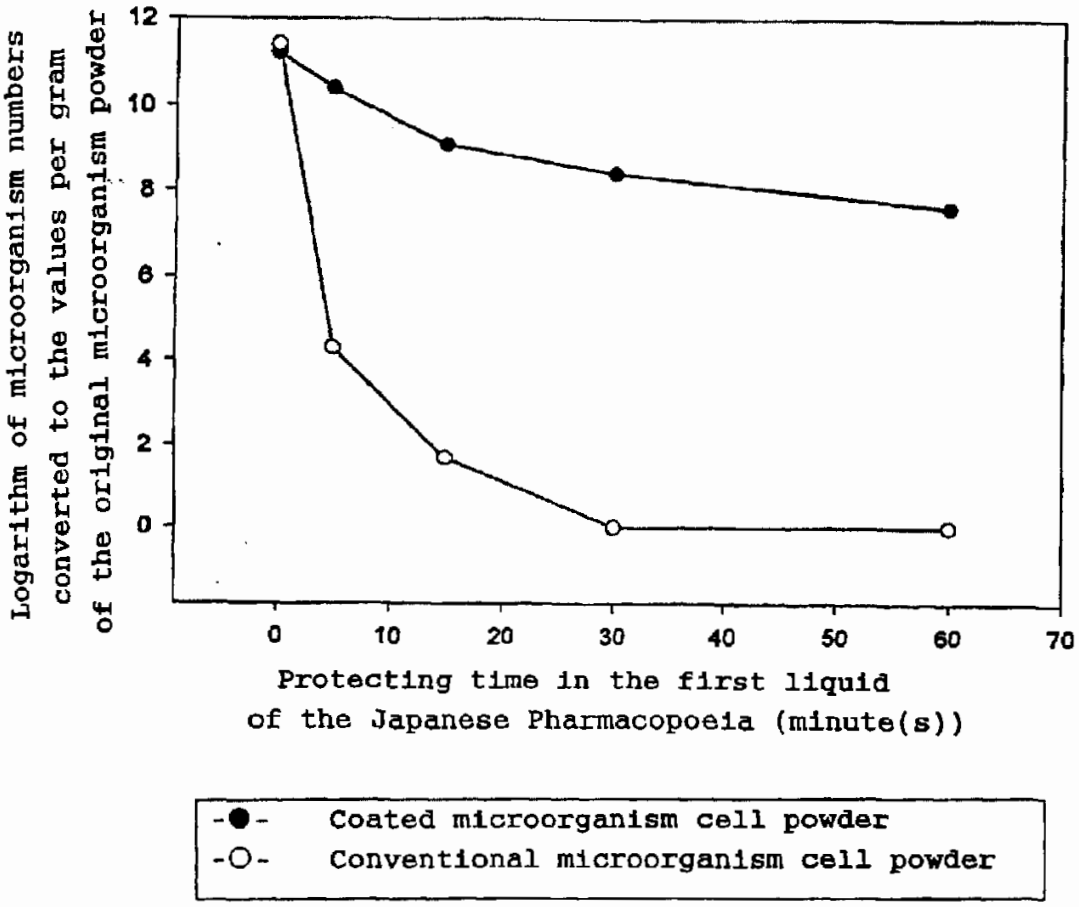
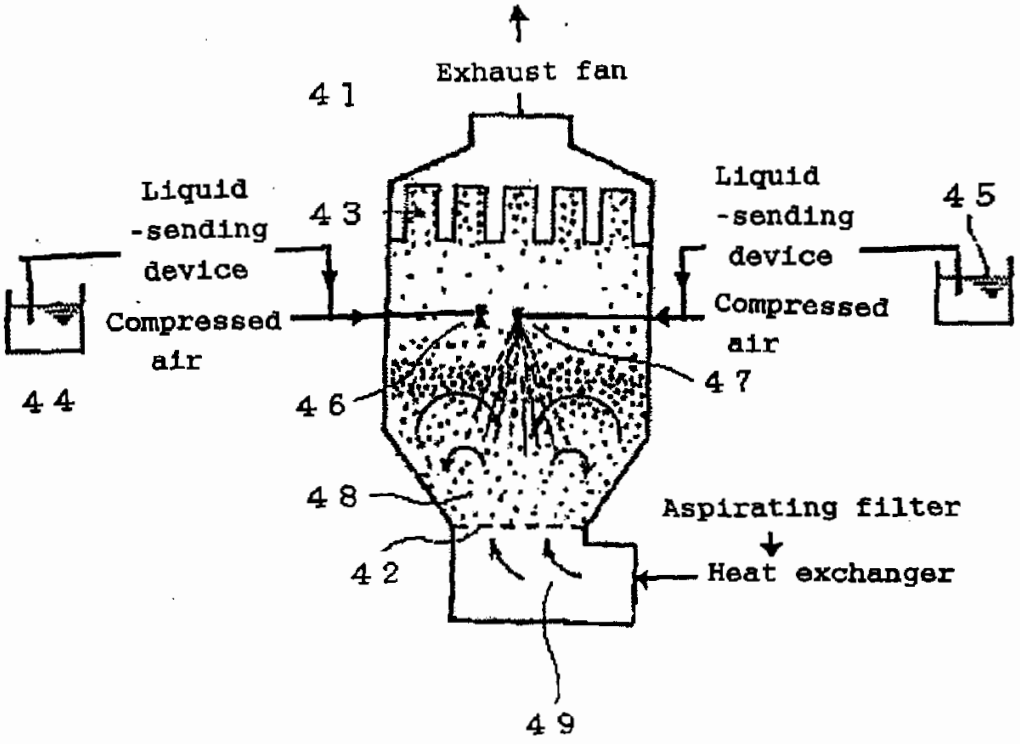

Logarithm of microorganism numbers converted to the values per gram of the original microorganism powder
12
10
8
6
4
2
0
0
10
20
30
40
50
60
70
Protecting time in the first liquid of the Japanese Pharmacopoeia (minute(s))
-●- Coated microorganism cell powder
-○- Conventional microorganism cell powder

Fig.4


Exhaust fan
41
Liquid
-sending
device
43
Compressed
air
44
Liquid
-sending
device
45
Compressed
air
46
47
48
Aspirating filter
42
Heat exchanger
49

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(54) Titre : PROCEDE DE SECHAGE PAR PULVERISATION POUR PREPARER UNE POUDRE DETERGENTE SECHEE PAR PULVERISATION DE FAIBLE DENSITE, AVEC PEU D'ADJUVANT, HAUTEMENT SOLUBLE DANS L'EAU

(54) Title: A SPRAY-DRYING PROCESS FOR PREPARING A LOW DENSITY, LOW BUILDER, HIGHLY WATER-SOLUBLE SPRAY-DRIED DETERGENT POWDER

(57) Abrégé/Abstract:
The present invention relates to a spray-drying process for the preparation of a spray- dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0wt% to 10wt% zeolite builder and from 0wt% to 10wt% phosphate builder, and wherein the process comprises the step of: (a) preparing an aqueous slurry suitable for spray-drying comprising from 30wt% to 60wt% water and from 40wt% to 70wt% non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component, wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3: 1 to 5: 1; and (b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65°C to 140°C, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70°C to 120°C.

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(54) Title: A SPRAY-DRYING PROCESS FOR PREPARING A LOW DENSITY, LOW BUILDER, HIGHLY WATER-SOLUBLE SPRAY-DRIED DETERGENT POWDER

(57) Abstract: The present invention relates to a spray-drying process for the preparation of a spray- dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0wt% to 10wt% zeolite builder and from 0wt% to 10wt% phosphate builder, and wherein the process comprises the step of: (a) preparing an aqueous slurry suitable for spray-drying comprising from 30wt% to 60wt% water and from 40wt% to 70wt% non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component, wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3: 1 to 5: 1; and (b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65°C to 140°C, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70°C to 120°C.

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A SPRAY-DRYING PROCESS FOR PREPARING A LOW DENSITY, LOW BUILDER, HIGHLY WATER-SOLUBLE SPRAY-DRIED DETERGENT POWDER

FIELD OF THE INVENTION

The present invention relates to a spray-drying process for the preparation of a low density, low builder, highly water-soluble spray-dried powder. The spray-dried powder is suitable for use as a solid laundry detergent composition, or for incorporation into a solid laundry detergent composition. The spray-drying process comprises the step of spray-drying an aqueous slurry comprising a large amount of water. The conditions of the spray-drying process promote steam puffing; which in turn leads to the formation of spray-dried detergent powder having a very low bulk density. The spray-dried detergent powder exhibits excellent solubility upon contact with water, even in cold water temperatures, such as 20°C or lower.

BACKGROUND OF THE INVENTION

In recent years, the manufacturers of solid laundry detergent products have focused their efforts into formulating highly water-soluble laundry detergent compositions that exhibit a good cleaning performance and a good dissolution performance in water. Some examples of these efforts are described in: DE19912679 and WO03/038028, both by Henkel KGaA; EP1416039 and EP1416040, both by Dalli-Werke Wasche und Korperflege GmbH & Co.KG; and WO05/083046, WO05/083048, WO05/083049, WO06/020788, WO06/020789, WO06/088665, WO06/088666, EP1690921 and EP1690922, all by The Procter & Gamble Company.

These attempts typically remove a large proportion of the composition, namely the zeolite and/or phosphate builder, and preferably at least some sulphate salt. This in turn means that a lower dosage of the composition during the laundering process is required. However, many consumers do not want to dose a smaller volume of detergent during their laundering process. Therefore, there remains a need to significantly reduce the bulk density of these low builder laundry detergent compositions. This in turn enables the consumer to dose the same volume of these low builder laundry detergents they have used in the past for the more

conventional high builder laundry detergents, during their laundering process. The use of low builder laundry detergent powders, due to their improved solubility in water, enables lower washing temperatures to be used, which improves the environmental and economic cost of the laundering process.

SUMMARY OF THE INVENTION

The Inventors have overcome the above problem of by providing a spray-drying process according to claim 1.

DETAILED DESCRIPTION OF THE INVENTION

Spray-drying process. The spray-drying process comprises the steps of preparing an aqueous slurry, and spraying the aqueous slurry into a spray-drying tower.

Typically, the aqueous slurry is prepared at a temperature in the range of from 60°C to 80°C. Typically the liquid ingredients, including ingredients in the form of a hot-melt, such as chelants, polymeric carboxylates, linear alkyl benzene sulphonate, that make up the aqueous slurry, including the water, are pre-heated to a temperature in the range of from 60°C to 80°C.

Preferably, essentially all of the detersive surfactant, if present, is contacted to the water before essentially any polymer is contacted to the water. Preferably essentially all of the polymer, if present, is contacted to the water before essentially any inorganic material. This is especially preferred as it ensures the optimal phase chemistry of the aqueous slurry for spray-drying.

Typically, the temperature of the aqueous slurry as it enters the spray-drying tower is in the range of from 50°C to 140°C, preferably from 60°C, or from 70°C, and preferably to 120°C, or to 99°C or to 95°C or to 90°C, or to 85°C, or even to 80°C.

Typically, the outlet air temperature of the spray-drying tower is in the range of from 50°C to 200°C, preferably from 60°C, or from 70°C or even 80°C, and preferably to 140°C, or to 120oC, or to 99oC or to 95°C or to 90°C, or even to 85°C.

Typically, the air flow rate in the spray-drying tower is in the range of from $1m^3s^{-1}$ to $40m^3s^{-1}$, preferably from $5m^3s^{-1}$, or from $10m^3s^{-1}$ or from $15m^3s^{-1}$ or even from $20m^3s^{-1}$, and preferably to $35m^3s^{-1}$, or even to $30m^3s^{-1}$.

Typically, the maximum cross-sectional area of the spray-drying tower is in the range of from $2m^2$ to $70m^2$, preferably from $10m^2$, or from $20m^2$, or from $30m^2$, or from $40m^2$, and preferably to $60m^2$.

Typically, the ratio of (i) the air flow rate in the spray-drying tower to (ii) the maximum cross-sectional area of the spray-drying tower is in the range of from $0.15ms^{-1}$ to $4ms^{-1}$, preferably from $0.2ms^{-1}$, or from $0.3ms^{-1}$, or even from $0.4ms^{-1}$, and preferably to $3ms^{-1}$, or to $2ms^{-1}$, or to $1ms^{-1}$, or even to $0.75ms^{-1}$. This is especially preferred in order to control the residency time of the aqueous slurry in the spray-drying tower so as to ensure adequate drying time. This is even more preferred when it is desirable to spray-dry at lower air temperatures.

Typically, the aqueous slurry is sprayed into the spray-drying tower through at least one nozzle, preferably multiple nozzles, having an aperture in the range of from 2mm to 5mm, preferably from 3mm, or from 3.5mm, and preferably to 4mm.

Typically, the slurry is sprayed into the spray-drying tower at a pressure in the range of from 4.0×10^6 Nm^{-2} to 9.0×10^6 Nm^{-2}, preferably from 5.0×10^6 Nm^{-2}, and preferably to 7.0×10^6 Nm^{-2}, or even to 6.0×10^6 Nm^{-2}. These pressures, especially these low pressures, promote steam puffing, which in turn lead to the formation of spray-dried detergent powder having a very low density.

Typically, the ratio of (i) the rate in gs^{-1} units at which the aqueous slurry is sprayed into the spray-drying tower to (ii) the maximum cross-sectional area in m^2 units of the spray-drying tower is in the range of from $3gm^{-2}s^{-1}$ to $3{,}000gm^{-2}s^{-1}$, preferably from $20gm^{-2}s^{-1}$, or from $40gm^{-2}s^{-1}$, or even from $60gm^{-2}s^{-1}$, and preferably to $2{,}000gm^{-2}s^{-1}$, or to $1{,}000gm^{-2}s^{-1}$, or to $500gm^{-2}s^{-1}$, or to $250gm^{-2}s^{-1}$, or even to $150gm^{-2}s^{-1}$. This is especially preferred in order to control the residency time of the aqueous slurry in the spray-drying tower so as to ensure adequate drying time. This is even more preferred when it is desirable to spray-dry at lower air temperatures.

Spray-dried detergent powder. The spray-dried detergent powder has a bulk density of 426g/l or less, preferably from 100g/l, and preferably of 400g/l or less, or 300g/l or less, or even 200g/l or less. The method for determining the bulk density of the spray-dried powder is described in more detail below.

Typically, the spray-dried detergent powder comprises anionic detersive surfactant, from 0wt% to 10wt% zeolite builder, from 0wt% to 10wt% phosphate builder, preferably from 0wt% to 10wt% silicate salt. Typically, the spray-dried detergent powder comprises a

polymeric carboxylate and carbonate salt. The anionic detersive surfactant, zeolite builder, phosphate builder, silicate salt, polymeric carboxylate, and carbonate salt are described in more detail below.

Typically, the spray-dried detergent powder is suitable for use as, or for incorporation into, a solid laundry detergent composition. The spray-dried powder can be admixed with other detergent ingredients, such as dry-added sodium percarbonate, anionic detersive surfactant agglomerates, enzymes or other spray-dried powders, to form a solid laundry detergent composition.

Typically, the spray-dried detergent powder comprises a polymeric component and a non-polymeric component. The polymeric component and non-polymeric component are described in more detail below. Typically, and even preferably, the spray-dried detergent powder comprises an inorganic component and an organic component. The inorganic component and organic component are described in more detail below.

Aqueous slurry. The aqueous slurry is suitable for spray-drying. The aqueous slurry comprises from 30wt% to 60wt% water, preferably from 35wt%, or from 40wt%, or from 45wt%, or even from 50wt% water, and preferably to 55wt% water. The aqueous slurry comprises from 40wt% to 70wt% non-aqueous material, preferably from 45wt%, and preferably to 65wt%, or to 60wt%, or to 55wt%, or even to 50wt% non-aqueous material. The non-aqueous material means any material that is not water. The non-aqueous material is described in more detail below.

The aqueous slurry has a viscosity of from 0.2Pas to 2.0Pas, when measured at a shear rate of 1,000s^{-1} and at a temperature of 70°C.

Non-aqueous material. The non-aqueous material is any material that is not water. The non-aqueous material typically comprises an inorganic component and an organic component. The inorganic component and organic component are described in more detail below. Typically, the non-aqueous material comprises an inorganic component and organic component in a weight ratio of from 0.1:1 to 10:1, preferably from 0.2:1, or even from 0.3:1, and preferably to 5:1, or to 3:1, or to 1.5:1, or to 1.2:1, or to 1.0:1, or to 0.8:1, or even to 0.5:1.

The non-aqueous material typically comprises a polymeric component and a non-polymeric component.

Typically, the non-aqueous material comprises anionic detersive surfactant, polymeric carboxylate and carbonate salt. The anionic detersive surfactant, polymeric carboxylate, and carbonate salt are described in more detail below. It may be preferred that the non-aqueous material comprises from 0wt% to 5wt% alkyl alkoxylated sulphate anionic detersive surfactant, preferably to 4wt%, or to 3wt%, or to 2wt%, or to 1wt% alkyl alkoxylated sulphate anionic detersive surfactant.

It may even be preferred that the non-aqueous material comprises essentially no alkyl alkoxylated sulphate anionic detersive surfactant; by comprises essentially no alkyl alkoxylated sulphate anionic detersive surfactant it is meant that the non-aqueous material comprises no deliberately added alkyl alkoxylated sulphate anionic detersive surfactant. This is especially preferred if the non-aqueous material comprises an alkyl benzene sulphonate anionic detersive surfactant.

Typically, the non-aqueous material comprises from 0wt% to 10wt% zeolite builder, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% zeolite builder. It may even be preferred for the non-aqueous material to be essentially free from zeolite builder. By essentially free from zeolite builder it is typically meant that the non-aqueous material comprises no deliberately added zeolite builder.

Typically, the non-aqueous material comprises from 0wt% to 10wt% phosphate builder, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% phosphate builder. It may even be preferred for the non-aqueous material to be essentially free from phosphate builder. By essentially free from phosphate builder it is typically meant that the non-aqueous material comprises no deliberately added phosphate builder.

Typically, the non-aqueous material comprises from 0wt% to 10wt% silicate salt, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% silicate salt. It may even be preferred for the non-aqueous material to be essentially free from silicate salt. By essentially free from silicate salt it is typically meant that the non-aqueous material comprises no deliberately added silicate salt.

Inorganic component: For the purpose of the present invention, inorganic component is defined as any material that does not comprise a hydrocarbon moiety. Examples of inorganic component include sodium carbonate and sodium sulphate.

Organic component: For the purpose of the present invention, organic component is defined as any material that comprises a hydrocarbon moiety. For the purpose of the present invention, a hydrocarbon moiety comprises a carbon atom that is covalently bonded to a hydrogen atom; i.e. having the general formula:



Examples of organic component include alkyl benzene sulphonate and citric acid.

Polymeric component. For the purpose of the present invention, the polymeric component is defined as any material that comprises at least four monomer units and has a molecular weight of 1,000 Da or greater.

Non-polymeric component. For the purpose of the present invention, the non-polymeric component is defined as any material that comprises less than four monomer units and/or has a molecular weight of less than 1,000 Da.

Anionic detersive surfactant: The spray-dried powder typically comprises from 1wt% to 70wt% anionic detersive surfactant, preferably from 2wt%, or from 5wt%, or from 7wt%, or even from 10wt%, and preferably to 60wt%, or to 50wt%, or to 40wt%, or even to 30wt% anionic detersive surfactant. Suitable anionic detersive surfactants are alkoxylated alcohol sulphate anionic detersive surfactants such as linear or branched, substituted or unsubstituted ethoxylated C_{12-18} alcohol sulphates having an average degree of ethoxylation of from 1 to 10, preferably from 3 to 7. Other suitable anionic detersive surfactant are alkyl benzene sulphonate anionic detersive surfactants such as linear or branched, substituted or unsubstituted C_{8-18} alkyl benzene sulphonates, preferably linear unsubstituted C_{10-13} alkyl benzene sulphonates. Other suitable anionic detersive surfactants are alkyl sulphates, alkyl sulphonates, alkyl phosphates, alkyl phosphonates, alkyl carboxylates or any mixture thereof.

Polymeric carboxylate. The spray-dried powder preferably comprises polymeric carboxylate. It may be preferred for the spray-dried powder to comprise at least 1wt%, or at least 2wt%, or at least 3wt%, or at least 4wt%, or even at least 5wt% polymeric carboxylate. The polymeric carboxylate can sequester free calcium ions in the wash liquor. The polymeric

carboxylate can also act as a soil dispersant and can provide an improved particulate stain removal cleaning benefit. Preferred polymeric carboxylates include: polyacrylates, preferably having a weight average molecular weight of from 1,000Da to 20,000Da; co-polymers of maleic acid and acrylic acid, preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 1:1 to 1:10 and a weight average molecular weight of from 10,000Da to 200,000Da, or preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 0.3:1 to 3:1 and a weight average molecular weight of from 1,000Da to 50,000Da.

Carbonate salt. The spray-dried powder typically comprises carbonate salt, typically from 1wt% to 50wt%, or from 5wt% to 25wt% or from 10wt% to 20wt% carbonate salt. A preferred carbonate salt is sodium carbonate and/or sodium bicarbonate. A highly preferred carbonate salt is sodium carbonate. Preferably, the spray-dried powder may comprise from 10wt% to 40wt% sodium carbonate. However, it may also be preferred for the spray-dried powder to comprise from 2wt% to 8wt% sodium bicarbonate. Sodium bicarbonate at these levels provides good alkalinity whilst minimizing the risk of surfactant gelling which may occur in surfactant-carbonate systems. If the spray-dried powder comprises sodium carbonate and zeolite builder, then preferably the weight ratio of sodium carbonate to zeolite builder is at least 15:1.

The carbonate salt, or at least part thereof, is typically in particulate form, typically having a weight average particle size in the range of from 200 to 500 micrometers. However, it may be preferred for the carbonate salt, or at least part thereof, to be in micronised particulate form, typically having a weight average particle size in the range of from 4 to 40 micrometers; this is especially preferred when the carbonate salt, or at least part thereof, is in the form of a co-particulate admixture with a detersive surfactant, such as the alkyl benzene sulphonate, or alternatively with an alkoxylated anionic detersive surfactant.

High levels of carbonate improve the cleaning performance of the spray-dried powder by increasing the pH of the wash liquor. This increased alkalinity: improves the performance of the bleach, if present; increases the tendency of soils to hydrolyze, which facilitates their removal from the fabric; and also increases the rate, and degree, of ionization of the soils to be cleaned (n.b. ionized soils are more soluble and easier to remove from the fabrics during the washing stage of the laundering process). In addition, high carbonate levels improve the flowability of the spray-dried powder.

Zeolite builder: The spray-dried detergent powder typically comprises from 0wt% to 10wt% zeolite builder, preferably to 8wt%, or to 6wt%, or to 5wt%, or to 4wt% or to 2wt% zeolite builder. It may even be preferred for the spray-dried detergent powder to be essentially free from zeolite builder. By essentially free from zeolite builder it is typically meant that the spray-dried detergent powder comprises no deliberately added zeolite builder. This is especially preferred if it is desirable for the spray-dried detergent powder to be very highly water-soluble, to minimize the amount of water-insoluble residues (for example, which may deposit on fabric surfaces), and also when it is highly desirable to have transparent wash liquor. Zeolite builders include zeolite A, zeolite X, zeolite P and zeolite MAP.

Phosphate builder: The spray-dried detergent powder typically comprises from 0wt% to 10wt% phosphate builder, preferably to 8wt%, or to 6wt%, or to 5wt%, or to 4wt% or to 2wt% phosphate builder. It may even be preferred for the spray-dried detergent powder to be essentially free from phosphate builder. By essentially free from phosphate builder it is typically meant that the spray-dried detergent powder comprises no deliberately added phosphate builder. This is especially preferred if it is desirable for the spray-dried detergent powder to have a very good environmental profile. Phosphate builders include sodium tripolyphosphate.

Silicate salt: The spray-dried detergent powder preferably comprises from 0wt% to 10wt% silicate, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% silicate salt. It may even be preferred for the spray-dried detergent powder to be essentially free from silicate salt. By essentially free from silicate salt it is typically meant that the spray-dried detergent powder comprises no deliberately added silicate salt. This is especially preferred in order to ensure that the spray-dried detergent powder has a very good dispensing and dissolution profiles and to ensure that the spray-dried detergent powder provides a clear wash liquor upon dissolution in water. Silicate salts include water-insoluble silicates. Silicate salts include amorphous silicates and crystalline layered silicates (e.g. SKS-6). A typical silicate salt is sodium silicate.

Other detergent ingredients: The spray-dried powder, and the non-aqueous component of the aqueous slurry, typically comprises detergent ingredients. Suitable detergent ingredients include: detersive surfactants such as anionic detersive surfactants, nonionic

detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants; preferred non-ionic detersive surfactants are C_{8-18} alkyl alkoxylated alcohols having an average degree of alkoxylation of from 1 to 20, preferably from 3 to 10, most preferred are C_{12-18} alkyl ethoxylated alcohols having an average degree of alkoxylation of from 3 to 10; preferred cationic detersive surfactants are mono-C_{6-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides, more preferred are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C_{10-12} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride; source of peroxygen such as percarbonate salts and/or perborate salts, preferred is sodium percarbonate, the source of peroxygen is preferably at least partially coated, preferably completely coated, by a coating material such as a carbonate salt, a sulphate salt, a silicate salt, borosilicate, or mixtures, including mixed salts, thereof; bleach activator such as tetraacetyl ethylene diamine, oxybenzene sulphonate bleach activators such as nonanoyl oxybenzene sulphonate, caprolactam bleach activators, imide bleach activators such as N-nonanoyl-N-methyl acetamide, preformed peracids such as N,N-pthaloylamino peroxycaproic acid, nonylamido peroxyadipic acid or dibenzoyl peroxide; carbonate salts, preferably sodium carbonate and/or sodium bicarbonate, preferably sodium carbonate; polymeric carboxylates, preferably co-polymers of maleic acid and acrylic acid and salts thereof; enzymes such as amylases, carbohydrases, cellulases, laccases, lipases, oxidases, peroxidases, proteases, pectate lyases and mannanases; suds suppressing systems such as silicone based suds suppressors; fluorescent whitening agents; photobleach; filler salts such as sulphate salts, preferably sodium sulphate; fabric-softening agents such as clay, silicone and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4-vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as hydrophobically modified cellulose and oligomers produced by the condensation of imidazole and epichlorhydrin; soil dispersants and soil anti-redeposition aids such as alkoxylated polyamines and ethoxylated ethyleneimine polymers; anti-redeposition components such as carboxymethyl cellulose and polyesters; perfumes; sulphamic acid or salts thereof; citric acid or salts thereof; and dyes such as orange dye, blue dye, green dye, purple dye, pink dye, or any mixture thereof.

Preferably, the composition comprises less than 1wt% chlorine bleach and less than 1wt% bromine bleach. Preferably, the composition is essentially free from bromine bleach and

chlorine bleach. By "essentially free from" it is typically meant "comprises no deliberately added".

Method for determining the bulk density of the spray-dried powder. The bulk density is typically determined by the following method:

Summary: A 500 ml graduated cylinder is filled with a powder, the weight of the sample is measured and the bulk density of the powder is calculated in g/l.

Equipment:

1. Balance. The balance has a sensitivity of 0.5g.

2. Graduated cylinder. The graduated cylinder has a capacity 500ml. The cylinder should be calibrated at the 500ml mark, by using 500g of water at 20°C. The cylinder is cut off at the 500ml mark and ground smooth.

3. Funnel. The funnel is cylindrical cone, and has a top opening of 110mm diameter, a bottom opening of 40mm diameter, and sides having a slope of 76.4° to the horizontal.

4. Spatula. The spatula is a flat metal piece having of a length of at least 1.5 times the diameter of the graduated cylinder.

5. Beaker. The beaker has a capacity of 600ml.

6. Tray. The tray is either a metal or plastic square, is smooth and level, and has a side length of at least 2 times the diameter of the graduated cylinder.

7. Ring stand.

8. Ring clamp.

9. Metal gate. The metal gate is a smooth circular disk having a diameter of at least greater than the diameter of the bottom opening of the funnel.

Conditions: The procedure is carried out indoors at conditions of 20°C temperature, $1 \times 10^5 Nm^{-2}$ pressure and a relative humidity of 25%.

Procedure:

1. Weigh the graduated cylinder to the nearest 0.5g using the balance. Place the graduated cylinder in the tray so that it is horizontal with the opening facing upwards.

2. Support the funnel on a ring clamp, which is then fixed to a ring stand such that the top of the funnel is horizontal and rigidly in position. Adjust the height of the funnel so that its bottom position is 38mm above the top centre of the graduated cylinder.

3. Support the metal gate so as to form an air-tight closure of the bottom opening of the funnel.

4. Completely fill the beaker with a 24 hour old powder sample and pour the powder sample into the top opening of the funnel from a height of 2cm above the top of the funnel.

5. Allow the powder sample to remain in the funnel for 10 seconds, and then quickly and completely remove the metal gate so as to open the bottom opening of the funnel and allow the powder sample to fall into the graduated cylinder such that it completely fills the graduated cylinder and forms an overtop. Other than the flow of the powder sample, no other external force, such as tapping, moving, touching, shaking, etc, is applied to the graduated cylinder. This is to minimize any further compaction of the powder sample.

6. Allow the powder sample to remain in the graduated cylinder for 10 seconds, and then carefully remove the overtop using the flat edge of the spatula so that the graduated cylinder is exactly full. Other than carefully removing the overtop, no other external force, such as tapping, moving, touching, shaking, etc, is applied to the graduated cylinder. This is to minimize any further compaction of the powder sample.

7. Immediately and carefully transfer the graduated cylinder to the balance without spilling any powder sample. Determine the weight of the graduated cylinder and its powder sample content to the nearest 0.5g.

8. Calculate the weight of the powder sample in the graduated cylinder by subtracting the weight of the graduated cylinder measured in step 1 from the weight of the graduated cylinder and its powder sample content measured in step 7.

9. Immediately repeat steps 1 to 8 with two other replica powder samples.

10. Determine the mean weight of all three powder samples.

11. Determine the bulk density of the powder sample in g/l by multiplying the mean weight calculated in step 10 by 2.0.

EXAMPLES

Example 1. A spray-dried laundry detergent powder and process of making it.

Aqueous slurry composition.

Component	%w/w Aqueous slurry
Linear alkyl benzene sulphonate	10.6
Acrylate/maleate copolymer	4.6
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	1.4
Sodium carbonate	19.4
Sodium sulphate	28.6
Water	34.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	1.4
Total Parts	**100.00**

Preparation of a spray-dried laundry detergent powder.

An aqueous slurry having the composition as described above is prepared having a moisture content of 34.0%. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. At the end of preparation, the aqueous slurry is heated to 80°C and pumped under pressure ($5x10^6 Nm^{-2}$), into a counter current spray-drying tower with an air inlet temperature of from 290°C. The aqueous slurry is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.15mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 2.0wt%, a bulk density of 310g/l and a particle size distribution such that greater than 90wt% of the spray-dried powder has a particle size of from 150 to 710 micrometers. The composition of the spray-dried powder is given below.

Spray-dried laundry detergent powder composition.

Component	%w/w Spray Dried Powder
Linear alkyl benzene sulphonate	15.8
Acrylate/maleate copolymer	6.8
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	2.1
Sodium carbonate	28.7
Sodium sulphate	42.4
Water	2.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	2.2
Total Parts	**100.00**

Example 2. A spray dried laundry detergent powder and process of making it.

Aqueous slurry composition.

Component	%w/w Aqueous slurry
Linear alkyl benzene sulphonate	21.3
Acrylate/maleate copolymer	9.4
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	1.7
Sodium carbonate	18.8
Carboxy-methyl-cellulose polymer	4.3
Water	42.0
Miscellaneous such as magnesium sulphate, brightener, and one or more stabilizers	2.5
Total Parts	**100.00**

Preparation of a spray-dried laundry detergent powder.

An aqueous slurry having the composition as described above is prepared having a moisture content of 42.0%. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. At the end of preparation, the

aqueous slurry is heated to 85°C and pumped under pressure (from $6.5x10^6Nm^{-2}$), into a counter current spray-drying tower with an air inlet temperature of from 275°C. The aqueous slurry is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.15mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 3.0wt%, a bulk density of 250g/l and a particle size distribution such that greater than 90wt% of the spray-dried powder has a particle size of from 150 to 710 micrometers. The composition of the spray-dried powder is given below.

Spray-dried laundry detergent powder composition.

Component	**%w/w Spray Dried Powder**
Linear alkyl benzene sulphonate	35.7
Acrylate/maleate copolymer	15.7
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	2.9
Sodium carbonate	31.4
Carboxy-methyl-cellulose polymer	7.1
Water	3.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	4.2
Total Parts	**100.00**

CLAIMS

1. A spray-drying process for the preparation of a spray-dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0wt% to 10wt% zeolite builder and from 0wt% to 10wt% phosphate builder, and wherein the process comprises the step of:

(a) preparing an aqueous slurry suitable for spray-drying comprising from 30wt% to 60wt% water and from 40wt% to 70wt% non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component, wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3:1 to 5:1; and

(b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65°C to 140°C, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70°C to 120°C.

2. A process according to claim 1, wherein the aqueous slurry comprises from 40wt% to 50wt% water and from 50wt% to 60wt% non-aqueous material.

3. A process according to any preceding claim, wherein the spray-dried detergent powder has a bulk density of 325g/l or less.

4. A process according to any preceding claim, wherein the air flow rate in the spray-drying tower is in the range of from $15m^3s^{-1}$ to $30m^3s^{-1}$, wherein the maximum cross-sectional area of the spray-drying tower is in the range of from $20m^2$ to $40m^2$,
and wherein the ratio of (i) the air flow rate in m^3s^{-1} units in the spray-drying tower to (ii) the maximum cross sectional area of the spray-drying tower in m^2 units is in the range of from $0.2ms^{-1}$ to $1.0ms^{-1}$.

5. A process according to any preceding claim, wherein the slurry is sprayed into the spray-drying tower through a nozzle having an aperture having a diameter in the range of from 3mm to 4mm.

6. A process according to any preceding claim, wherein the slurry is sprayed into the spray-drying tower at a pressure in the range of from 5.0 x 10^6 Nm^{-2} to 7.0 x 10^6 Nm^{-2}.

7. A process according to any preceding claim, wherein the ratio of (i) the rate in gs^{-1} units at which the aqueous slurry is sprayed into the spray-drying tower to (ii) the maximum cross-sectional area in m^2 units of the spray-drying tower is in the range of from 40 to 250$gm^{-2}s^{-1}$.

8. A process according to any preceding claim, wherein the non-aqueous material comprises anionic surfactant, polymeric carboxylate and carbonate salt, wherein:

(a) the weight ratio of anionic surfactant to polymeric carboxylate is in the range of from 2:1 to 3:1;

(b) the weight ratio of carbonate salt to anionic surfactant is in the range of from 0.5:1 to 2:1; and

(c) the weight ratio of carbonate salt to polymeric carboxylate is in the range of from 1.5:1 to 4:1.

9. A process according to any preceding claim, wherein the non-aqueous material comprises alkyl benzene sulphonate anionic detersive surfactant.

10. A process according to any preceding claim, wherein the non-aqueous material comprises from 0wt% to 4wt% silicate salt.

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Description

Xanthan and other microbial polysaccharides are made initially by fermentation as very dilute aqueous solutions. Even at very low concentrations these solutions are very viscous. Typically the consistency index of the solutions is above 25,000 cP. Very concentrated solutions therefore cannot easily be handled and when it is necessary to increase the solids content it is conventional to provide the polysaccharide in solid form by precipitation from its solution and then drying the precipitate.

The precipitation and drying is technically quite difficult to conduct and inevitably results in some deterioration in product quality, probably due to hornification or partial insolubilisation during drying. The particulate product generally has a relatively wide range of coarse particle sizes, for instance with the average particle size being 200 microns or greater and with 90% by weight of the particles having a range of sizes of at least 150 and usually 200 microns or more.

The fermentation broth generally consists of the aqueous solution but it is proposed in Canadian Patent Specification 1,164,376 to conduct the fermentation in an emulsion in oil of the dilute aqueous solution. Other emulsion fermentation processes are described in EP 0058364 and U.S. 4,352,882. The oil must be relatively non-volatile in order that unacceptable quantities are not lost due to the passage of oxygen through the oil during fermentation. The emulsion must be relatively unstable in order that, at the end of fermentation, it can be broken, optionally by addition of an emulsion breaking agent, by high shear, by heating, dilution, or evaporation or other known methods, and the xanthan is then separated from the aqueous phase, optionally after purification, by conventional means such as precipitation and drying. Thus the final product quality is similar to that made by conventional aqueous broth fermentation processes. It is significant that although the process is said to result in enhanced yields the concentration of xanthan in the resultant aqueous solution is still very low, not more than 2.5% by weight in the Examples.

As is discussed more fully in EP 0128661 (not published at the priority date of this application), it is desirable that the polysaccharide should dissolve easily and quickly and should rapidly provide its maximum viscosifying power, particularly for enhanced oil recovery, drilling mud or other downhole use, but existing dried products tend to be rather unsatisfactory despite various published attempts to improve solution rate. In general, a choice has to be made between the use of a viscous dilute aqueous solution (with its associated bulk and handling disadvantages) and solids (with the resultant inferior performance properties). Other processes that have been published since the priority date of this application are described in EP 0130891 and EP 137538.

It has been our object to formulate polysaccharides, and in particular xanthan and other microbial polysaccharides, in a form that has convenience and handling properties the same as or approaching conventional powder form and that has performance qualities better than those of existing solid grade products, preferably approaching or as good as the performance qualities of the solution grade product. This objective has not previously been possible or proposed in the polysaccharide industry, except as described above.

It is known in the synthetic polymer industry to obtain a water-in-oil fluid dispersion of aqueous particles of water soluble polymer dispersed in oil by dispersing an aqueous solution of monomer in oil and then polymerising the monomer. There are numerous proposals in the literature, for instance U.S. 4,052,353, describing drying the resultant dispersion by azeotroping to form a fluid dispersion of substantially dry particles dispersed in oil. In GB 905,779 it is mentioned that a dispersion of aqueous synthetic polymer particles in oil can be spray-dried.

The possibility of granulating an aqueous gel of a polymer in oil has been recognised (for instance in GB 1,277,577) but, as is admitted in that specification, this involves the handling of thick gels and the use of shearing machinery which increases the cost of manufacturing considerably. Also the application of shear to an aqueous gel is liable to damage the polymeric structure, with the result that there is a risk that the performance qualities will again be decreased. This is a particular problem if a fine dispersion, as opposed to a coarse granular product is desired. Accordingly it is recognised that it is not satisfactorily possible to form the water-in-oil polymer dispersion starting from a solution of the polymer and in practice the water in oil polymer dispersion is always made by in situ polymerisation.

It is known from examples 13 and 14 of U.S. 3,979,349 to disperse, respectively, 20% aqueous gelatin and 10% aqueous polyvinyl alcohol in oil but these solutions are unusual polymeric solutions in that they have much lower viscosity than most water soluble polymers and so dispersion can be achieved by such low shear, for instance simple stirring, that there is no danger of damaging the polymer. For instance a typical 10% aqueous polyvinyl alcohol solution may have a consistency index below 3,000 cP. These solutions therefore are entirely different from the aqueous polymers that the industry has accepted can not conveniently be dispersed into oil and are entirely different from the very viscous polysaccharide solutions that at present are used for, for instance, enhanced oil recovery.

As described in EP 0128661 we have found that it is possible to form an emulsion in oil of an aqueous polysaccharide solution having a consistency index that is so high that one would not expect to be able conveniently and satisfactorily to emulsify it into water, for instance above 10,000 or 20,000 cP and often above 50,000 cP, using conventional and economically acceptable dispersing apparatus and that this can be done

without causing significant damage to the final properties of the polysaccharide. That application is concerned with the production of liquid compositions and describing how the emulsion can be made more concentrated. The described concentration method involves azeotropic distillation.

In the present invention we are not concerned with the concentration of an emulsion but are instead concerned with the production of polysaccharide in substantially dry, powder form.

In the invention, we spray dry an emulsion in a non-aqueous liquid of an aqueous solution of a polysaccharide and thereby produce polysaccharide powder substantially free of non-aqueous liquid. During the spray-drying the non-aqueous liquid is substantially entirely evaporated and so we do not obtain a concentrated emulsion but, instead, we can obtain solid substantially dry particles as a powder. Surprisingly they can easily have uniform particle size and have very desirable characteristics. The product, spray dried polysaccharide (preferably microbial polysaccharide), is novel.

The emulsion of aqueous polysaccharide in non-aqueous liquid is usually free of cell debris, e.g., as a result of being formed from isolated material that is free of such debris. However the emulsion can contain cell debris and may be an emulsion formed by fermentation in oil, e.g., as in any of the emulsion fermentation patents quoted above. The concentration of the aqueous phase is then quite low, e.g., down to 1%.

It is desirable, when conducting a spray-drying process, to minimise the capital and energy requirements. It is therefore commercially desirable that the concentration of polysaccharide in the emulsion and in the aqueous component should be as high as possible consistent with ability to handle it and to disperse it into oil, so as to maximise the polysaccharide solids put into the dispersion. Although the invention can be conducted when the solution only has a concentration typical of xanthan fermentation broth, e.g., 1 to 2.5% maximum, for economic reasons it is preferred that the concentration of the polysaccharide in the aqueous solution that is in the emulsion should be at least 4% by weight, preferably at least 5% and most preferably 7 to 10% or sometimes more, for instance up to 15% or even 20%, depending upon the polysaccharide.

The aqueous dispersion that is to be spray dried preferably contains from 30 to 75%, preferably 50 to 75% by weight aqueous phase with the balance being the non-aqueous phase.

This means that the polysaccharide content of the emulsion will always be quite low, usually above 1% but below 10 or 15%, typically 2 to 6% by weight. Higher concentrations are difficult to achieve because of, for instance, the difficulty of emulsification. Spray drying of dilute liquids normally gives hollow crushable particles, and therefore a wide range of particle sizes and it is surprising that in the invention it is possible to obtain solid particles of a narrow range of particle sizes despite the low concentration of the emulsion.

The emulsion is normally made by emulsification of a solution that may be obtained in any convenient manner. Preferably it is a concentrate obtained from the broth in which the microbial polysaccharide is initially prepared. However in some instances it is useful to form the solution by dissolving powder in water e.g. when it is desired to facilitate the production, by a user, of an aqueous solution that is more concentrated than can conveniently be made from powder.

The emulsion is preferably formed by emulsifying preformed aqueous solution into oil, but the polysaccharide solution may, alternatively, be formed in water droplets previously emulsified into oil. The aqueous solution that is emulsified into non-aqueous liquid is preferably a concentrate obtained from a fermentation broth. Although the invention can be applied to a wide range of polysaccharides, and therefore to solutions having a wide range of viscosities, it is of particular value when the polysaccharide solution has a consistency index above 10,000 cP, and preferably above 20,000 cP, but solutions of lower viscosity can be used. The consistency index may be above 50,000 and is often 100,000 or more, for instance up to half a million, cP. For instance a typical 7% Xanthan solution may have a consistency index of about 66,000 cP.

The emulsification of the polysaccharide solution can be conducted using conventional emulsifying apparatus, with the aqueous solution generally being added gradually to the non-aqueous phase. The degree of shear and emulsification will affect the particle size of the emulsion. The solution may include alkali, generally ammonia, to raise the pH up to, for instance, 9 or 10. The solution is generally free of formaldehyde, since its presence may cause uncontrolled cross-linking.

The non-aqueous liquid can be any liquid which is immiscible with the aqueous phase and which is volatile such that it can subsequently be removed during spray drying. It is generally a mineral oil, diesel oil, vegetable oil, or a halogenated hydrocarbon. Examples of suitable liquids are perchlorethylene and commercially available hydrocarbons with boiling ranges below 250°C and preferably below 150°C, but generally above 50°C, most preferably within the range 70 to 150°C. Halogenated hydrocarbons such as perchlorethylene and other non-aqueous liquid that have a higher density than conventional aliphatic low boiling hydrocarbons are desirable since they facilitate the production of a stable emulsion with low quantities of surfactant and/or stabiliser, or in the total absence of surfactant and/or stabiliser.

Polar liquids may be included in the emulsion (generally by admixture with the oil) to facilitate emulsification and/or to improve stability of the composition and/or to act as a humectant for the polysaccharide. Glycols, for instance ethylene glycol, and glycol ethers are suitable.

The emulsion must be sufficiently stable that it

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does not break before spray drying. The emulsion may be formed immediately before spray drying, in which event storage stability is not required. It may even be formed at the spraying nozzle with simultaneous emulsification and spraying. Alternatively the emulsion may be made and then stored, in which event it must be storage stable in the sense that the aqueous phase remains emulsified throughout the oil or, if the aqueous phase tends to settle, then it must be easy to emulsify it back into the oil.

Surfactant may be included to facilitate reduction of particle size and/or to improve stability. Surfactants that will serve as water in oil emulsifiers generally have a low HLB value at 20°C while surfactants that have high HLB values normally lead to the formation of an oil in water emulsion or to the formation of a very unstable emulsion. Although surfactants having, e.g. HLB of 3 to 6 can be used in the invention the emulsion is preferably formed using a surfactant which serves as a water in oil emulsifier during the formation of the emulsion but which at 20°C has an HLB value of at least 6.5, generally at least 7 and typically 8 to 11, preferably 9.5 to 10.5. Some of these high HLB surfactants are water in oil emulsifiers at 20°C and so can be used at ambient temperatures. Other high HLB surfactants are oil in water emulsifiers at ambient temperatures but become water in oil emulsifiers when heated to above their phase inversion temperature. With such emulsifiers it is then desirable to form the emulsion above the phase inversion temperature of the surfactant.

Preferably the emulsion is, at some stage during or after its preparation, at a temperature of at least 50°C, e.g. 50 to 120°C and preferably 75 to 95°C. Thus hot oil may be added to cold solution or hot solution may be added to cold oil or cold oil and cold solution may be mixed and the mixture heated to the desired temperature above 50°C either during emulsification or after the formation of the emulsion. This heating step is of particular value when the emulsion includes a surfactant that is an oil-in-water emulsifier at ambient temperatures but a water-in-oil emulsifier at higher temperatures.

The surfactants are generally nonionic. Preferably they are ethyleneoxide condensates of sorbitan esters or of sorbitol esters but other suitable surfactants are glycol esters and ethyleneoxide condensates of nonyl or other alkyl phenols, ethylene oxide condensates of fatty alcohols or acids and ethyleneoxide propyleneoxide copolymers. Mixtures may be used.

The preferred materials are ethoxylated sorbitan monooleate (e.g. Tween 81, containing 5 ethoxy groups and HLB about 10), ethoxylated sorbitol septaoleate (e.g. Arlatone T, containing about 40 ethoxy groups and HLB about 9.5) and polyethylene glycol oleates. Suitable low HLB surfactants include sorbitan esters such as Span 80 (sorbitan monooleate, HLB about 4.3). Span, Tween and Arlatone are trade marks.

The amount of surfactant, if present, is generally from 0.1 to 5%, preferably 0.3 to 2%, by weight of the oil phase or 0.01 to 1% by weight of the emulsion.

Stabiliser may be included to stabilise the emulsion, especially if it is to be stored before use. Suitable stabilisers are oil soluble polymeric stabiliser and preferably are amphipathic copolymers of one or more hydrophobic monomers with one or more hydrophillic monomers. The hydrophobic monomers may be acrylates such as C_8 to C_{24}, optionally together with C_1 and C_4, alkyl esters of acrylic or methacrylic acid, for instance ceto-stearyl or stearyl methacrylate, optionally copolymerised with methyl methacrylate. The hydrophilic monomers, may be anionic, cationic or non-ionic, preferably being methacrylic acid or other acrylic monomer. Examples of preferred stabilisers are described in GB 1,482,515. The preferred stabilisers are copolymers of ceto stearyl methacrylate and methacrylic acid containing 60-70% molar of the methacrylate ester. Other polymeric stabilisers include polyhydroxy stearic acid-polyethylene glycol condensates, for instance with oleic acid, and maleic polymers such as those described in U.S. 4,339,371.

The amount of stabiliser, if present, is generally from 0.1 to 5%, preferably 0.3 to 2% by weight of the oil phase or 0.01 to 1% by weight of the emulsion. The ratio of surfactant to stabiliser may be from 1:3 to 3:1.

The emulsion can be spray dried under conditions that will give a powder and using conventional spray drying apparatus provided with means for collecting evaporated non-aqueous liquid and generally provided with means for supplying nitrogen through the spray dryer as the drying medium. Typically the inlet temperature for the spray drying nitrogen or other gas is from 120 to 200°C, preferably around 150°C, and the outlet temperature is from 50 to 100°C, preferably around 70°C.

The conditions of spray drying must be such that substantially all the non-aqueous liquid is evaporated, and in particular such that the final product does not contain a continuous phase of non-aqueous liquid but is either totally free of it or possibly has a small residue on each particle.

The conditions of drying must also be such that the product is a dry powder. Thus the water content of the polysaccharide particles is reduced sufficiently that the particles do not undesirably stick to each other when they are collected in the spray drier or subsequently handled. The maximum water content that can be tolerated in the spray dried particles will depend upon, for instance, the amount of stabiliser since the presence of a significant amount of stabiliser will prevent or minimise sticking of relatively high water content particles. The amount of water in each particle must generally be minor, based on the weight of polysaccharide and water and is normally less than 30%, generally below 25% and preferably below 10%. Best results are generally obtained when the water content is in the region 5 to 10%.

The nozzle by which the emulsion is sprayed into the spray dryer is usually an atomiser rotating at high speed, for instance above 20,000 rpm typically 30,000 to 70,000 rpm. The described emulsions can easily be sprayed by conventional apparatus to form fine particles which dry during their passage through the spray dryer. This is in contrast to what happens if an attempt is made to spray dry even a very dilute solution of Xanthan. For instance even at 2% concentration such a solution causes strings in the spray dryer nozzle and will either block the apparatus or will, at best, give a product of very non-uniform size.

The size of the polysaccharide particles obtained by spray drying appears to depend primarily upon the particle size in the emulsion but may also depend, in some processes, upon the degree of atomisation in the spray dryer. In many processes it appears that the size of the final dry polysaccharide particles will be strongly influenced by, and will generally be the same as, the dry particle size of the aqueous polysaccharide particles in the emulsion and so may depend upon the emulsification conditions. Even if the size is influenced by the spraying conditions a great advantage of the spray drying process is that it is possible, for the first time, to obtain a powdered polysaccharide having a narrow range of particle sizes and it is also possible to obtain, for the first time, a powdered polysaccharide having a narrow and small range of particle sizes.

It may be necessary to sieve the product from the spray dryer in order to remove grossly oversized particles. The total amount of them in the product is generally less than 5%.

By the invention it is possible to obtain a powdered polysaccharide which has at least 90% by weight of the particles within a particle size range of not more than 100 microns and preferably not more than 75 microns, and preferably at least 75% by weight of the particles are within a particle size range of not more than 50 microns. The average particle size can be selected at will by selection of the emulsification and spraying conditions.

These powdered polysaccharides conveniently fall into one of two classes. One class have an average particle size above 50 microns, but generally below 250 microns and can, for convenience, be termed beads. Preferably the average particle size is from 70 or 100 microns to 150 or 200 microns. Preferably at least 90% by weight of the beads are below 200 microns in size. Their production generally requires the initial formation of a very coarse particle size emulsion, for instance an emulsion that contains little or no emulsifier, for instance below 1% or 0.8%, and often below 0.5%, by weight of the emulsion.

The other class of powdered polysaccharide that can be made by the invention is much finer and has an average particle size below 50 microns and generally above 10 microns, preferably from 20 to 40 microns. At least 90%, and preferably at least 95% by weight of the particles have a size below 100 microns and preferably below 75 microns. Preferably at least 75% by weight of the particles have a size below 70 microns, and preferably below 50 microns. Preferably at least 50% by weight of the particles have a size below 60 microns, preferably below 40 microns.

These powdered polysaccharides are very advantageous compared to conventional powdered polysaccharides (having a wide range of particle sizes) because their narrow particle size distribution greatly facilitates putting them into solution by mixing with water.

The individual particles of polysaccharide are preferably coated with surfactant or stabiliser that will promote the distribution of the particles into water, upon addition with water. The surfactant and/or stabiliser conveniently is a residue from the emulsion and so may be any of the materials mentioned above but the surfactants whose HLB decreases with decreasing temperature are particularly preferred in this respect.

A further advantage of the very fine particulate polysaccharides, having an average particle size below 50 microns, is that the fine particles permit much more rapid dissolution into water than conventional polysaccharides, which have always contained significant quantities of larger particles. However when handling the very fine polysaccharide powder dusting can be a problem and mixing into water can be difficult. Preferably therefore the fine powder is dispersed into a non-aqueous liquid.

The powders made in the invention can be used to provide a polysaccharide dispersion which comprises a dispersion in non-aqueous liquid of the powdered polysaccharide of which at least 90% and preferably at least 95% by weight of the particles have a size below 100 microns, the average particle size of the particles preferably being below 50 microns, the preferred maximum particle sizes and average particle sizes all being as discussed above. Preferably the particles are coated with surfactant or stabiliser, as discussed above. The dispersion is made by mixing into the non-aqueous liquid polysaccharide powder made by the spray drying technique described above.

The non-aqueous liquid may be any liquid in which the polysaccharide does not swell unacceptably and so may be polar or non-polar. It is generally preferred to use a relatively non-volatile hydrocarbon oil.

The dispersion should be substantially stable, in that the particles either stay permanently suspended in the non-aqueous liquid or can easily be resuspended by stirring. With an appropriate choice of liquid and a very small particle size adequate stability may be attainable without any additives in the dispersion. Often however it is desirable to add a dispersion stabiliser, for instance a material that will have the effect of thickening the continuous phase. The stabiliser may therefore be a synthetic polymer that will thicken the aqueous phase or an inorganic material, such as a clay, for instance bentone clay or other organophilic clay. The total amount of stabiliser in the dispersion is preferably below

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10% by weight of the dispersion, most preferably below 5% by weight. Suitable non-aqueous liquids and suspending agents are described in, for instance, EP 39128 but in the invention much lower amounts of stabiliser will be required than are recommended in that since the particles are much smaller.

The dispersion should be water-dispersable so that the polysaccharide can be dissolved into water simply by dispersing the dispersion into water and exposing the dispersed particles to the bulk water. The process of dispersion is facilitated by the application of shear or, particularly, by the provision of a surfactant that will act as an oil in water emulsifier. The high HLB surfactants discussed above will generally serve for this purpose during the dissolution stage especially if they required heating during emulsification, and their use is particularly advantageous. However it may be desirable to include a conventional oil-in-water surfactant for promoting the distribution of the dispersion into water and the dissolution of the polysaccharide particles. Suitable amounts are from 1 to 5% by weight of the dispersion. This may be added to the dissolving water, or to the dispersion and may be included during its preparation or immediately prior to use. The surfactant preferably has HLB 7-11 at room temperature.

The dispersion of dry polysaccharide in oil preferably contains from 30 to 75%, preferably 50 to 75% by weight dry polysaccharide with the balance being non-aqueous liquid containing, if necessary, dispersion stabiliser.

The invention is of particular value when the polysaccharide is a Xanthan, for instance as obtained by fermentation of Xanthamonas or is other microbial polysaccharide having, for instance, viscosity characteristics rather similar to Xanthans, i.e. dilute solutions of, for instance, 4% have a consistency index above 20,000 cP, and in particular the polysaccharides obtained by fermentation of Pseudomonas. However the invention is of value with all microbial polysaccharides (commonly referred to as biopolymers) and other polysaccharides such as starch and derivatives thereof, water soluble cellulose derivatives, galactomannon gums, plant exudates and algal gums such as alginate and carrageenan. The preferred polysaccharides give a 4% aqueous solution having a consistency index above 20,000 cPs.

The invention is of value wherever these or other polysaccharides have to be provided in powdered solid or fluid concentrated form with maximum retention of activities. Suitable downhole uses for Xanthans and other polysaccharides include drilling muds, workover fluids and other well stimulation fluids, completion fluids, and for providing water retention in cement, especially when the polysaccharide is a cellulose ether such as carboxymethyl hydroxyethyl cellulose. The compositions can also be used in any other situation where it is necessary to present the polysaccharide in high concentration and with high activity, and especially when it is required to provide a composition which will readily dissolve into water to form a viscous solution.

Although it is generally desirable that the polysaccharide remains uncross-linked, if cross-linking and partial insolubilisation is required a small amount of glyoxal or other appropriate cross-linking agent may be included either in the aqueous emulsion that is to be spray dried or in the final dry dispersion.

The following are non-limiting examples of the invention.

EXAMPLE 1

227 parts by weight of a very viscous (consistency index above 50000 cPs) aqueous solution obtained by dissolving 7 parts Xanthan powder in 100 parts water is emulsified into an oil phase consisting of 95 parts Shell Solvent 41, 1 part Tween 81 (surfactant HLB 10) and 1 part of a stabiliser formed of 2:1 molar copolymer of cetostearyl methacrylate and methacrylic acid). The emulsion is formed by homogenisation using a Silverson Mixer at 80°C for 15 minutes and allowed to cool. The emulsion is stable for standing for at least 4 weeks.

This emulsion is then spray dried in a spray drying tower provided with solvent recovery apparatus and under conditions that produce a product that is a powder. The atomiser by which the emulsion is sprayed into the tower rotates at 45,000 rpm. Nitrogen is passed through the tower at an inlet temperature of 150°C and an outlet temperature of 70°C.

The resultant powder is passed through a 700 micron sieve to remove about 5% by weight large flakes, above 2 mm in size. The remainder has a particle size distribution 100% by weight below 90 microns, about 90% below 50 microns, about 75% below 40 microns, about 50% below 30 microns and about 20% below 20 microns and about 2% below 10 microns.

55 parts by weight of this powder is stirred slowly into 43 parts Shell Pale Oil 60 thickened with 2 parts organophilic clay (Bentone SD) and is then stirred rapidly for 5 minutes with a Hamilton Beach Mixer. The product is a stable suspension that does not settle over several days. Its viscosity measured on a Brookfield RVT Spindle 3 at 0.5 rpm is 13,000 cP, at 5 rpm 2,760 cP and at 100 rpm 668 cP.

A solution of the xanthan in water is obtained by mixing this dispersion into water, optionally in the presence of oil-in-water emulsifier in the water or in the dispersion.

EXAMPLE 2

In a modification of the process of Example 1, beads having particle sizes mainly in the range 90 to 150 μ are obtained if the amount of Tween 81 is reduced or eliminated or if the aqueous phase is blended into the oil phase by vigorous stirring rather than by homogenisation. The resultant beads can be screened to remove oversize particles and, if necessary, can be sieved to reduce their range of particle sizes. They are free flowing

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and can easily be stirred into water to form a solution.

EXAMPLE 3

The process of Example 1 may be repeated using, instead of a solution obtained from Xanthan powder and water, a concentrate obtained by fermentation of Xanthomonas or Pseudomonas followed by purification and concentration in known manner to give a polysaccharide concentration of about 7% and a consistency index above 50,000 cps.

Claims

1. A process of making a dry powdered polysaccharide characterised in that the process comprises spray drying an emulsion in a non-aqueous liquid of an aqueous solution of the said polysaccharide and thereby substantially entirely evaporating the non-aqueous liquid and producing the powdered polysaccharide substantially free of non-aqueous liquid.

2. A process according to claim 1 comprising forming the emulsion by emulsifying an aqueous solution of polysaccharide having consistency index above 20,000 cPs into the non-aqueous liquid, and then spray drying the said emulsion and thereby producing powdered polysaccharide substantially free of non-aqueous liquid.

3. A process according to claim 1 or claim 2 in which the polysaccharide content of the emulsion is from 1 to 15% and the water content of the powdered product is below 10% by weight.

4. A process according to any preceding claim in which the emulsion is stabilised by the presence therein of a stabilising component selected from water-in-oil emulsifiers having HLB below 11 and amphipathic copolymeric stabilisers.

5. A process according to any preceding claim in which the polysaccharide is a microbial polysaccharide made by fermentation of a microorganism selected from Xanthomonas and Pseudomonas.

Patentansprüche

1. Verfahren zur Herstellung eines trockenen pulverisierten Polysaccharids, dadurch gekennzeichnet, daß das Verfahren die Sprühtrocknung einer Emulsion einer wäßrigen Lösung des Polysaccharids in einer nicht-wäßrigen Flüssigkeit umfaßt, wobei die nicht-wäßrige Flüssigkeit im wesentlichen vollständig verdampft wird und das pulverisierte Polysaccharid im wesentlichen frei von der nicht-wäßrigen Flüssigkeit hergestellt wird.

2. Verfahren nach Anspruch 1, umfassend die Bildung der Emulsion durch Emulgieren einer wäßrigen Lösung eines Polysaccharids mit einem Konsistenzindex oberhalb von 20000 cPs in der nicht-wäßrigen Flüssigkeit, und nachfolgend die Sprühtrocknung dieser Emulsion, wobei das pulverisierte Polysaccharid im wesentlichen frei von der nicht-wäßrigen Flüssigkeit hergestellt wird.

3. Verfahren nach Anspruch 1 oder 2, in dem der Polysaccharidgehalt der Emulsion im Bereich von 1 bis 15% und der Wassergehalt des pulverisierten Produktes unterhalb von 10 Gewichtsprozent liegen.

4. Verfahren nach einem der vorhergehenden Ansprüche, worin die Emulsion durch die Anwesenheit einer in ihr enthaltenen Stabilisierungskomponente stabilisiert wird, welche ausgewählt ist aus Wasser-in-Öl Emulgatoren mit einem HLB-Wert unter 11 und amphipathischen copolymeren Stabilisatoren.

5. Verfahren nach einem der vorhergehenden Ansprüche, in dem das Polysaccharid ein mikrobielles Polysaccharid ist, welches durch Fermentation eines Mikroorganismus, welcher ausgewählt ist aus Xanthomonas und Pseudomonas, hergestellt ist.

Revendications

1. Un procédé pour fabriquer un polysaccharide en poudre sec, caractérisé en ce que le procédé consiste à sécher par pulvérisation une émulsion d'une solution aqueuse dudit polysaccharide dans un liquide non aqueux et à évaporer ainsi pratiquement complètement le liquide non aqueux et à produire le polysaccharide en poudre pratiquement exempt de liquide non aqueux.

2. Procédé selon la revendication 1, qui consiste à former l'émulsion en émulsifiant dans le liquide non aqueux une solution aqueuse du polysaccharide ayant un indice de consistance de plus de 20 000 mPa.s et ensuite à sécher par pulvérisation ladite émulsion et à produire ainsi le polysaccharide en poudre pratiquement exempt de liquide non aqueux.

3. Procédé selon la revendication 1 ou 2, dans lequel la teneur en polysaccharide de l'émulsion est de 1 à 15% et la teneur en eau du produit en poudre est de moins de 10% en poids.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'émulsion est stabilisée par la présence dans celle-ci d'un composant stabilisant choisi parmi les émulsifiants huile-dans-l'eau ayant une HLB de moins de 11 et les stabilisants copolymères amphiphiles.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polysaccharide est un polysaccharide microbien fabriqué par fermentation par un microorganisme choisi parmi Xanthomonas et Pseudomonas.

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EP 0 227 486 B1

Description

The present invention relates to a spray drying process and an apparatus therefor.

Spray drying processes and apparatus therefor basically have three essential functions, namely, (1) spraying of a feed liquid to form microdrops, (2) drying of the microdrops to produce a powder and (3) separation and recovery of the powder product (see US-A-1512776, FR-A-441742 and GB-A-382129). These spray drying apparatus are ordinarily equipped with an atomizer, a drying chamber and a fine powder collector to perform each of said functions.

Examples of conventional spray drying apparatus are shown in Fig. 9 and Fig. 10. (Reference is made to JP-B-32601/1983 and JP-A-26950/1983).

In the spray drying apparatus of Fig. 9, in a drying chamber 1, a feed liquid is sprayed from a nozzle 5 and momentarily heated by hot gas (heated air) blown from a hot gas inlet 2, whereby the liquid component of the feed liquid is evaporated and the solid component is converted to a fine (dried) Powder. Most of the fine powder is taken out as a product through a rotary valve 6, but part of the fine powder is carried by an exhaust gas into a cyclone collector 7 (hereinafter referred to as "a cyclone") through a discharge gas outlet 3 and recovered from a rotary valve 8.

The spray drying apparatus of Fig. 10 is same as that of Fig. 9 except that as the atomizer, a rotary spraying disc 10 is used in place of the nozzle 5.

In the spray drying apparatus of the type as shown in Fig. 9 and Fig. 10, a fine powder as a product is recovered in two portions from the apparatus main body (drying chamber) and the cyclone, respectively. In this case, product particles having a heavier weight and larger particle diameters are taken out from the apparatus main body (drying chamber) and product particles having a lighter weight and smaller particle diameters from the cyclone. Hence, there occurs a slight nonuniformity in product composition.

This nonuniformity in product composition has hitherto presented no serious problem, depending upon the kind of the product.

There is now a demand for spray drying systems which produce a variety of products in small quantities, especially in the production of medicines and fine ceramics. With such systems a new problem has arisen in addition to the slight nonuniformity in product composition. This is that the systems require more frequent product changes and each change requires rapid and complete cleaning of solid which has adhered to the inner wall of the drying chamber. Such cleaning is necessary because (1) efficient operation of the systems requires a cleaning time as short as possible and (2) production of high purity and high quality products requires complete cleaning of an adhered solid at each product change. In actuality, complete cleaning is extremely difficult. Moreover, when the product is harmful to human bodies, direct contact with the product must be avoided making the cleaning very difficult.

Further, the slight nonuniformity in product composition has become a more serious problem in connection with the increased requirement for higher purity products.

The present invention seeks to provide a spray drying process suited for producing a wide variety of products in small quantities, especially fine powder products of high purity, as well as an apparatus therefor.

The invention provides in one aspect a process for producing a powder from a feed liquid, which process comprises spraying the feed liquid into a spray drying chamber formed by a single easily-detachable heat-resistant porous membrane having a funnel-shaped lower portion to form microdrops, introducing a hot gas into said chamber to dry said microdrops and form powder particles, withdrawing gas from said chamber through said porous membrane thereby to separate said powder particles from said gas, and removing said separated powder particles from said chamber through said funnel-shaped lower portion.

The invention also provides a spray drying apparatus for use in producing a powder from a feed liquid, which apparatus comprises a spray drying chamber having an inlet for hot gas, an outlet for discharge gas, an outlet for produced powder and spray means in said chamber for use in atomising the feed liquid into said hot gas in said drying chamber, characterised in that said chamber is formed by a single easily-detachable heat-resistant porous membrane having a funnel-shaped lower portion, said membrane being pervious to said gas but substantially impervious to said atomized feed liquid.

The present invention further provides a spray drying apparatus of integration type characterised by comprising a housing having an upper room and a lower room; in said upper room, two or more units for generation of a hot gas, two or more units for distribution of hot gas, two or more units for atomisation of feed liquid and at least one unit for discharge gas; in said lower room two or more moveably arranged units for recovery of produced powder; and between each feed liquid atomization unit in the upper room and each corresponding powder recovery unit in the lower room one spray drying chamber formed by a single easily-detachable heat-resistant porous membrane having a funnel-shaped lower portion.

The porous membrane used in the present invention preferably is bag-like or cylindrical. The mem-

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brane must be heat-resistant and preferably also has excellent powder releasability.

Hot gas is usually introduced into the spray drying chamber at an inlet temperature of 120° C to 280° C and leaves the chamber at an outlet temperature of 70° to 150° C; therefore, the porous membrane must withstand such a high temperature. Further, since a fine powder constantly adheres to and deposits on the porous membrane, the membrane preferably has excellent powder releasability in order to allow its continuous use. The porous membrane functions to separate fine powder product from the exhaust gas.

Any porous membrane having such characteristics can be used. However, there are ordinarily used fiber-made cloths, or laminates each consisting of two different such cloths. Preferably, there are used laminates of a powder-releasable, reticulate membrane and a woven or unwoven cloth as a reinforcing material. Preferable examples of the reticulate membrane are a membrane of polytetrafluoroethylene (PTFE) (brand name: Teflon) type and a polytrifluoroethylene type membrane, and preferable examples of the woven or unwoven cloth are cloths made from a polyimide, a heat-resistant nylon, a polyester or an aramid.

In the present invention, the whole of the spray drying chamber is formed by a single porous membrane. This makes detaching of the chamber easy and accordingly its maintenance very simple.

In a bag-like or cylindrical spray drying chamber formed by a porous membrane, a feed liquid is sprayed to form microdrops and the microdrops are momentarily dried by hot gas blown from its inlet and having an inlet temperature of 120° to 280° C to be converted into a fine powder and a gas. Some of the fine powder deposits on the bottom of the spray drying chamber under gravity, while the gas passes through the pores of the porous membrane, seperates from the rest of the fine powder, and is discharged through an outlet for exhaust gas. Hence, all of the fine powder is separated from the gas and, as a result, there occurs no nonuniformity in the composition of the fine powder product.

Continuous operation of the porous membrane causes adhesion and deposition of a fine powder to and on the membrane, leading to an increase in pressure drop and finally stoppage of operation. In order to avoid this, the fine powder needs be taken off as necessary. Since the porous membrane in general has excellent powder releasability, the adhered powder can be easily removed from the porous membrane in a short time by mechanical vibration, air injection from the opposite side (pulse air or reverse jet) or the like. When complete removal (cleaning) of the powder from the membrane without causing contamination with impurities is required, it can be done by replacing the porous membrane with a new one from outside without touching the product inside the membrane. This replacement is easy when the porous membrane has a bag-like shape.

Separation of a fine powder and a gas by the porous membrane is ordinarily conducted by passing a gas containing a fine powder through the meshes of the fiber constituting the porous membrane and allowing the fine powder to remain on the meshes. In actuality, however, this filtration is not simple. The meshes are usually many times as large as the particle sizes of the fine powder; accordingly, the fine powder is collected not only on the surface of the filtration cloth but also partially inside the cloth. In the present invention, such a filter cloth is used primarily for a fine powder of good solubility. Preferably, the porous membrane used in the present invention is a laminate of (1) a reticulate membrane as mentioned previously, having good powder releasability and capable of conducting surface filtration and (2) a woven or unwoven cloth as mentioned previously, of excellent heat resistance and strength as a carrier for the membrane (1). The effect of the present invention can be enhanced by the use of such a laminate. The diameters of the particles which can be captured by the porous membrane of the present invention can vary from 0.1 μm to several millimeters.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an example of the spray drying apparatus of the present invention. Fig. 1(a) is a schematic sectional view of the whole portion of the apparatus and Fig. 1(b) is a partially enlarges sectional view of the porous membrane used in the apparatus.

Fig. 2 to Fig. 5 are schematic sectional views showing other examples of the spray drying apparatus of the present invention.

Fig. 6 is a perspective view showing an example of the spray drying apparatus of integration type according to the present invention wherein each unit of the apparatus is accommodated in a housing.

Fig. 7 shows plan views of Fig.6, an example of the spray drying aratus of integration type according to the present invention wherein each unit of the apparatus is accommodated in a housing. Fig. 7(a) is a plan view of the upper room of the housing and Fig. 7(b) is a plan view of the lower room of the housing.

Fig. 8 is a drawing explaining an example of the operation of the spray drying apparatus of integration type according to the present invention wherein each unit of the apparatus is accommodated in a housing.

Fig. 9 and Fig. 10 are schematic sectional views showing conventional spray drying apparatuses.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Fig. 1 shows an embodiment of the spray drying apparatus of the present invention for carrying out the spray drying process of the present invention. Fig. 1(a) is a schematic sectional view of the whole portion of the apparatus and Fig. 1(b) is a partially enlarged sectional view of the porous membrane forming the spray drying chamber of the apparatus. In Fig. 1, a spray drying chamber 1 formed by a bag-like porous membrane 15 is arranged inside the main body 11 of the spray drying apparatus along the inner wall of the main body 11. As shown in Fig. 1(b), the porous membrane 15 is constituted by a laminate of a reticulate membrane 13 and a filter cloth 14 as a reinforcing material. Hot gas X is sent into the spray drying chamber 1 from the top of the main body 11 through an inlet 2 and is allowed to make counterflow contact with a feed liquid sprayed upward from the lower portion of the spray drying chamber 1 through a nozzle 5. A fine powder produced enters a product receiver (not shown) from an outlet 6 of seal valve type. A gas after drying is separated from a fine powder A via the porous membrane 15 forming the outer wall of the spray drying chamber 1 and is then discharged outside from a discharge gas outlet 3 installed at the lower portion of the main body 11.

Fig. 2 is a schematic sectional view showing another embodiment of the spray drying apparatus of the present invention. Fig. 2 is different from Fig. 1 in that a rotary spraying disc 10 is used as an atomizer, in place of the nozzle 5 and both hot gas X and a feed liquid from the rotary spraying disc 10 are introduced downward as parallel flows. In other respects, the structure of the apparatus of Fig. 2 is approximately same as that of Fig. 1.

Fig. 3 to Fig. 5 are schematic sectional views also showing other embodiments of the spray drying apparatus of the present invention. In Fig. 3, hot gas X and a feed liquid from a nozzle 5 are introduced downward as parallel flows. In Fig. 4, hot gas X and a feed liquid from a nozzle 5 are introduced upward as parallel flows. In Figs. 5(a) and (b), hot gas X and a feed liquid from a nozzle 5 are introduced from the side of the spray drying chamber 1.

In each of the apparatuses of Figs. 3 to 5, there is provided a blow-off mechanism Z (reverse jet and pulse air type) for blowing off a fine powder produced. For instance, pulse air is sent into a main body 11 from the opposite direction through a line 12, whereby a fine powder A which has adhered to a porous membrane 15 is blown off.

Fig. 6 and Fig. 7 each shows an embodiment of the spray drying apparatus of integration type according to the present invention wherein each unit of the apparatus is accommodated in a housing. Fig. 6 is a perspective view of the whole portion of the apparatus. Fig. 7(a) is a plan view of the upper room of the housing of the apparatus. Fig. 7(b) is a plan view of the lower room of the housing of the apparatus. In Figs. 6 and 7, a housing 16 consists of an upper room 17 and a lower room 18. In the upper room 17, there are arranged each three sets of units 19 for generation of hot gas, units 20 for distribution of hot gas and units 21 for atomization of feed liquid, as well as one common unit 22 for exhaust gas. In the lower room 18, there are arranged, below the feed liquid atomization units 21, the same sets (i.e. three sets) of units 23 for recovery of fine powder product. In the lower room 18, there are further arranged units 24a and 24b for blowing-off of fine powder and a unit 25 for preparation of feed liquid. Between the feed liquid atomization units 21 in the upper room and the corresponding fine powder recovery units 23 in the lower room, there are arranged the same sets (i.e. three sets) of spray drying chambers 1. A large number of bag-like porous members each to be used as a spray drying chamber 1 are stored in the lower room.

Referring to Fig. 8, there is explained the operation of the spray drying apparatus of integration type according to the present invention. The apparatus of Fig. 8 accommodates two sets of spray drying chambers for producing different products G and H. Explanation is made on one set. A feed liquid G_F supplied from a feed liquid preparation unit 25 through a pipe 27 is sprayed into a drying chamber 1 by a feed liquid atomization unit 21 to form microdrops, and the microdrops are momentarily dried by hot gas X blown from a hot gas generation unit 19 through a hot gas distribution unit, to be converted into a fine powder and a vapor. The fine powder is recovered as a product G_1 by a fine powder receiver 23. When the product to be produced next is G_2 or G_3 of different grade but similar to G_1, the porous membrane constituting the spray drying chamber 1 is removed and can be rapidly replaced by a porous membrane of exclusive use for G_2 or G_3 which is stored nearby. Another set is also operated in the basically same manner.

Meanwhile, the gas is separated from the fine powder through the pores of the porous membrane 26 and is discharged outside from a common discharge unit 22.

The spray drying apparatus and the apparatus therefor according to the present invention will be

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explained in more detail below by way of Examples.

(Example 1)

Using a spray drying apparatus of the type shown in Fig. 1, a feed liquid containing 60 % of stabilized zirconia ($Ca_{0.15}Zr_{0.85}O_{1.85}$) or 70 % of lanthanum-added barium titanate [$BaTiO_3$ + 0.01(La_2O_3)] was sprayed at a rate of 150 kg/hr. The drying chamber of the apparatus had dimensions of 2,500 mm in diameter, 2,500 mm in straight body height and 4,300 mm in total height, and had a cylindrical shape at the upper portion and a cone shape at the lower portion. The porous membrane forming the drying chamber was a laminate of a heat-resistant unwoven nylon cloth and a polytetrafluoroethylene. The inlet temperature of heated air was 220° C and the exhaust gas temperature was 120° C.

Under the above conditions, the spray drying operation of each feed liquid was conducted. As a result, the fine powder products obtained had the following properties.

	(1)	(2)
Average particle diameter	50 μm	60 μm
Water content	0.3 %	0.7 %
Nonuniformity in composition	None	None
Yield after 4 hours of operation	99 %	99 %

In the above, (1) refers to stabilized zirconia and (2) refers to lanthanum-added barium titanate.

The time required for product change was as short as about 40 minutes.

(Example 2)

Using a spray drying apparatus of the type shown in Fig. 8, a feed liquid containing 70 % of lanthanum-added barium titanate [$BaTiO_3$ + 0.01, 0.015 or 0.02 (La_2O_3)] was sprayed at a rate of 100 kg/hr. The drying apparatus was of G type. The drying chamber of the apparatus had dimensions of 2,000 mm in diameter, 500 mm in straight body height and 3,500 mm in total height, and had a cylindrical shape in the upper portion and a cone shape in the lower portion. The porous membrane forming the drying chamber was a laminate of a heat-resistant unwoven nylon cloth and a polytetrafluoroethylene. Each one membrane was used for each feed liquid.

The inlet temperature of heated air was about 220° C and the exhaust gas temperature was 120° C.

Under the above conditions, the spray drying operation of each feed liquid was conducted. As a result, the fine powder products had the following properties.

	(1)	(2)	(3)
Average particle diameter	50 μm	25 μm	50 μm
Water content	0.5 %	0.4 %	0.5 %
Nonuniformity in composition	None	None	None
Yield after 4 hours of operation	99 %	99 %	99 %

In the above, (1) refers tc the case of 0.01% lanthanum addition; (2) refers to the case of 0.015% lanthanum addition; and (3) refers to the case of 0.02% lanthanum addition.

The time required for product change was as short as about 30 minutes.

In this Example, cleaning at the time of product change was conducted only for the atomizer. The drying chamber was folded up and hanged down from a hook of exclusive use, so as to be able to be used in next drying.

As appreciated from the foregoing, the spray drying apparatus of the present invention uses a spray drying chamber formed by a porous membrane; as a result, there takes place no discharge, out of the apparatus, of the portion of a powder product having smaller particle diameters together with an exhaust gas, as experienced with the conventional spray drying apparatuses. Therefore, there is no nonuniformity in product composition; cleaning and blowing-off of adhered fine powder can be conducted rapidly and easily even in frequent product change inevitable with a more grade smaller quantity production system; as a result, a fine powder of higher quality and higher purity can be produced.

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In the spray drying apparatus of integration type according to the present invention wherein several spray drying chambers are accommodated in a housing, there are also arranged in the housing each several sets (each set has about the same size) of other necessary units such as hot gas generation units, hot gas distribution units and feed liquid atomization units and there are further stored in the housing a large number of porous membranes for each different product. Such a spray drying apparatus can provide the same performance as several tens of conventional spray drying apparatus, with a far smaller land area and a far lower facility cost.

As stated above, the spray drying process and apparatus of the present invention can produce a fine powder of high purity, is suited for use in producing a variety of products in small quantities, and accordingly can be utilized in the production of high purity products such as medicines and fine ceramics.

Claims

1. A spray drying process for producing a powder from a feed liquid, which process comprises spraying the feed liquid into a spray drying chamber (1) formed by a single easily-detachable heat-resistant porous membrane (15) having a funnel-shaped lower portion to form microdrops, introducing a hot gas (X) into said chamber to dry said microdrops and form powder particles, withdrawing gas from said chamber (1) through said porous membrane (15) thereby to separate said powder particles from said gas, and removing said separated powder particles from said chamber (1) through said funnel-shaped lower portion.

2. A spray drying process according to Claim 1, wherein the porous membrane (15) is bag-like or cylindrical.

3. A spray drying process according to Claim 1 or 2, wherein the porous membrane (15) comprises a laminate of (1) a powder-releasable, reticulate membrane (13) of surface filtration type and (2) a heat-resistant filter cloth (14) as a reinforcing material.

4. A spray drying apparatus for use in producing a powder from a feed liquid, which apparatus comprises a spray drying chamber (1) having an inlet (2) for hot gas (X), an outlet (3) for discharge gas, an outlet (6) for produced powder and spray means (5) in said chamber for use in atomizing the feed liquid into said hot gas in said drying chamber (1), characterized in that said chamber (1) is formed by a single easily-detachable heat-resistant porous membrane (15) having a funnel-shaped lower portion, said membrane being pervious to said gas but substantially impervious to said atomized feed liquid.

5. A spray drying apparatus according to Claim 4, wherein the porous membrane (15) is bag-like or cylindrical.

6. A spray drying apparatus according to Claim 4 or 5 wherein the porous membrane (15) comprises a laminate of (1) a powder-releasable, reticulate membrane (13) or surface filtration type and (2) a heat-resistant filter cloth (14) as a reinforcing material.

7. A spraying drying apparatus for use in producing a powder from a feed liquid, characterized in that the apparatus comprises a housing (16) having an upper room (17) and a lower room (18); in said upper room (17), two or more units (19) for generation of a hot gas, two or more units (20) for distribution of hot gas, two or more units (21) for atomization of feed liquid and at least one unit (22) for discharge gas; in said lower room (18) two or more moveably arranged units (23) for recovery of produced powder; and between each feed liquid atomization unit (21) in the upper room (17) and each corresponding powder recovery unit (21) in the lower room (18) one spray drying chamber (1) formed by a single easily-detachable heat-resistant porous membrane having a funnel-shaped lower portion.

8. A spray drying apparatus according to Claim 7, wherein the porous membrane is bag-like or cylindrical.

Revendications

1. Procédé de séchage par atomisation permettant de produire une poudre à partir d'un liquide alimentaire et comprenant les étapes suivantes : atomisation du liquide alimentaire à l'intérieur d'une chambre de séchage par atomisation (1) formée d'une membrane poreuse unique (15), résistant à la

chaleur et facilement détachable, dont la partie inférieure présente une forme d'entonnoir afin de produire des microgouttes ; introduction d'un gaz chaud (X) dans ladite chambre afin de sécher lesdites micro-gouttes et de produire les particules de poudre ; évacuation du gaz de ladite chambre (1) à travers ladite membrane poreuse (15) afin de séparer lesdites particules de poudre dudit gaz ; et évacuation desdites particules de poudre de ladite chambre (1) par ladite partie inférieure en forme d'entonnoir.

2. Procédé de séchage par atomisation selon la revendication 1, caractérisé en ce que la membrane poreuse (15) a la forme d'un sac ou d'un cylindre.

3. Procédé de séchage par atomisation selon la revendication 1 ou 2, caractérisé en ce que la membrane poreuse (15) se compose de (1) une membrane réticulée ne fixant pas la poudre (13) et de type à filtration de surface, et (2) un tissu filtrant résistant à la chaleur (14) en tant que matériau de renforcement.

4. Appareil de séchage par atomisation servant à produire une poudre à partir d'un liquide alimentaire, lequel appareil comprend une chambre de séchage par atomisation (1) présentant un orifice d'admission (2) pour le gaz chaud (X), un orifice d'échappement (3) pour le gaz d'évacuation, un orifice d'échappement (6) pour la poudre obtenue et des dispositifs d'atomisation (5) dans ladite chambre, servant à atomiser le liquide alimentaire dans ledit gaz chaud à l'intérieur de ladite chambre de séchage par atomisation (1), caractérisé en ce que la chambre (1) se compose d'une membrane poreuse unique (15), résistant à la chaleur et facilement détachable, dont la partie inférieure présente une forme d' entonnoir, ladite membrane étant perméable audit gaz mais essentiellement imperméable audit liquide alimentaire atomisé.

5. Appareil de séchage par atomisation selon la revendication 4, caractérisé en ce que la membrane poreuse (15) a la forme d'un sac ou d'un cylindre.

6. Appareil de séchage par atomisation selon la revendication 4 ou 5, caractérisé en ce que la membrane poreuse (15) se compose de (1) une membrane réticulée ne fixant pas la poudre (13) et de type à filtration de surface, et (2) un tissu filtrant résistant à la chaleur (14) en tant que matériau de renforcement.

7. Appareil de séchage par atomisation servant à produire une poudre à partir d'un liquide alimentaire, caractérisé en ce que l'appareil comprend un bâti (16) composé d'une enceinte supérieure (17) et d'une enceinte inférieure (18) ; ladite enceinte supérieure (17) contient au moins deux unités (19) de production de gaz chaud, au moins deux unités (20) de distribution du gaz chaud, au moins deux unités (21) d'atomisation du liquide alimentaire et au moins une unité (22) d'évacuation du gaz ; ladite enceinte inférieure (18) contient au moins deux unités (23) mobiles de récupération de la poudre produite ; et entre chaque unité d'atomisation de liquide alimentaire (21) de l'enceinte supérieure (17) et chaque unité de récupération de poudre correspondante (21) de l'enceinte inférieure (18) se trouve une chambre de séchage par atomisation (1) formée par une membrane poreuse unique, résistant à la chaleur et facilement détachable, dont la partie inférieure présente une forme d'entonnoir.

8. Appareil de séchage par atomisation selon la revendication 7, caractérisé en ce que la membrane a la forme d'un sac ou d'un cylindre.

Patentansprüche

1. Sprühtrocknungsverfahren zur Herstellung eines Pulvers aus einer eingespeisten Flüssigkeit mit folgenden Verfahrensschritten: Sprühen der eingespeisten Flüssigkeit in eine Sprühtrocknungskammer (1), die durch eine einzelne einfach herausnehmbare und hitzebeständige poröse Membran (15) gebildet ist und einen unteren trichterförmigen Teil aufweist, zur Bildung von Mikrotropfen, Einleiten eines heißen Gases (X) in die Kammer, um die Mikrotropfen zu trocknen und feine Pulverpartikel zu bilden, Abziehen des Gases aus der Kammer (1) durch die poröse Membran (15), wobei die Pulverpartikel von dem Gas getrennt werden und Abziehen der abgetrennten Pulverpartikel aus der Kammer (1) durch den trichterförmigen unteren Teil.

2. Sprühtrocknungsverfahren nach Anspruch 1, in welchem die poröse Membran (15) taschenförmig oder zylindrisch ausgebildet ist.

3. Sprühtrocknungsverfahren nach Anspruch 1 oder 2, in welchem die poröse Membran (15) ein Laminat aus einer 1. Pulver freigebenden, netzartigen Membran (13) vom Typ eines Oberflächenfilters und 2. ein hitzeresistentes Filtertuch (14) als Verstärkungsmaterial umfaßt.

4. Sprühtrocknungsvorrichtung zur Erzeugung eines Pulvers aus einer eingespeisten Flüssigkeit mit einer Sprühtrocknungskammer (1) mit einem Einlaß (2) für Heißgas (X), einem Auslaß (3) für ausströmendes Gas, einen Auslaß (6) für das hergestellte Pulver und Sprühmittel (5) in der Kammer zum Atomisieren der eingespeisten Flüssigkeit in der Sprühtrocknungskammer (1) in das heiße Gas hinein, dadurch gekennzeichnet, daß die Kammer (1) durch eine einzeine leicht herausnehmbare und hitzebeständige poröse Membran (15) gebildet ist, die einen trichterförmigen unteren Teil aufweist, wobei die Membran für das Gas durchlässig aber für die atomisierte eingespeiste Flüssigkeit im wesentlichen undurchlässig ist.

5. Sprühtrocknungsvorrichtung nach Anspruch 4, in welchem die poröse Membran (15) taschenförmig oder zylindrisch ausgebildet ist.

6. Sprühtrocknungsvorrichtung nach Anspruch 4 oder 5, in welcher die poröse Membran (15) ein Laminat aus einer 1. Pulver freigebenden, netzartigen Membran (13) vom Typ eines Oberflächenfilters und 2. ein hitzeresistentes Filtertuch (14) als Verstärkungsmaterial umfaßt.

7. Sprühtrocknungsvorrichtung zur Herstellung eines Pulvers aus einer eingespeisten Flüssigkeit, dadurch gekennzeichnet, daß die Vorrichtung ein Gehäuse (16) mit einem oberen Raum (17) und einem unteren Raum (18) umfaßt, wobei in dem oberen Raum (17) zwei oder mehr Einheiten (19) zur Erzeugung eines Heißgases angeordnet sind, zwei oder mehr Einheiten (20) zur Verteilung des Heißgases, zwei oder mehr Einheiten (21) zur Atomisierung der eingespeisten Flüssigkeit und zumindest eine Einheit (22) für ausströmendes Gas und wobei in dem unteren Raum (18) zwei oder mehr beweglich angeordnete Einheiten (23) zur Gewinnung des erzeugten Pulvers angeordnet sind und wobei zwischen dieser Atomisierungseinheit (21) für die eingespeiste Flüssigkeit im oberen Raum (17) und jeder entsprechenden Pulvergewinnungseinheit (21) im unteren Raum (18) eine Sprühtrocknungskammer (1) angeordnet ist, welche durch eine einzelne einfach herausnehmbare und hitzebeständige poröse Membran gebildet ist, die einen trichterförmigen unteren Teil aufweist.

8. Sprühtrocknungsvorrichtung nach Anspruch 7, in welchem die poröse Membran taschenförmig oder zylindrisch ausgestaltet ist.

FIG. 1

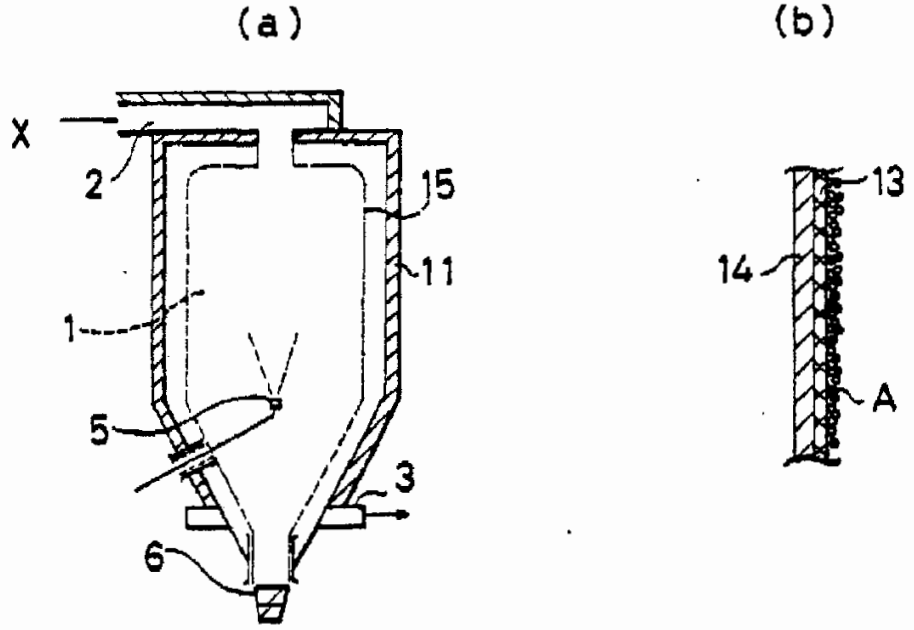
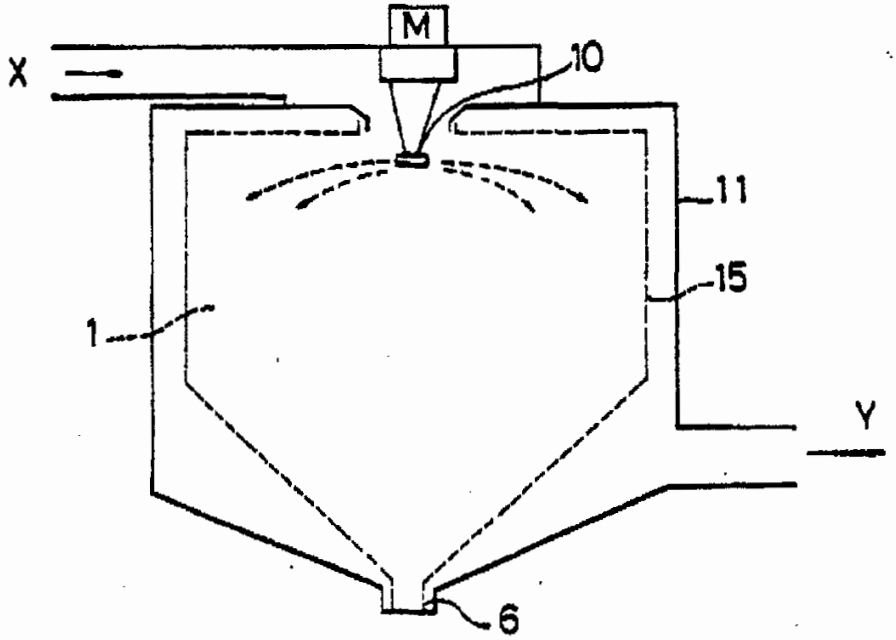


FIG. 2



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FIG. 3

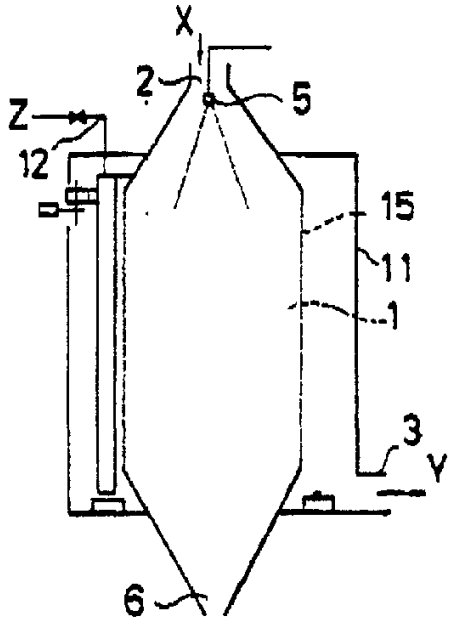


FIG. 4

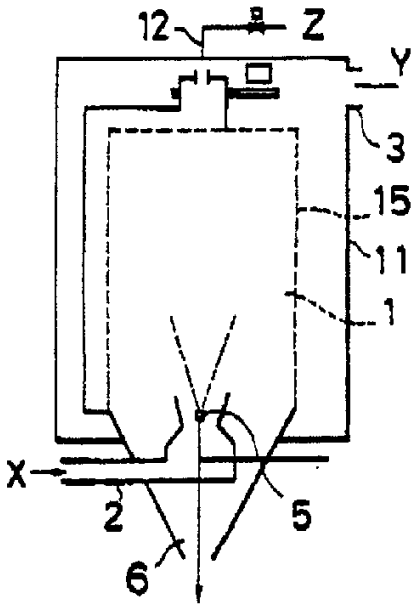
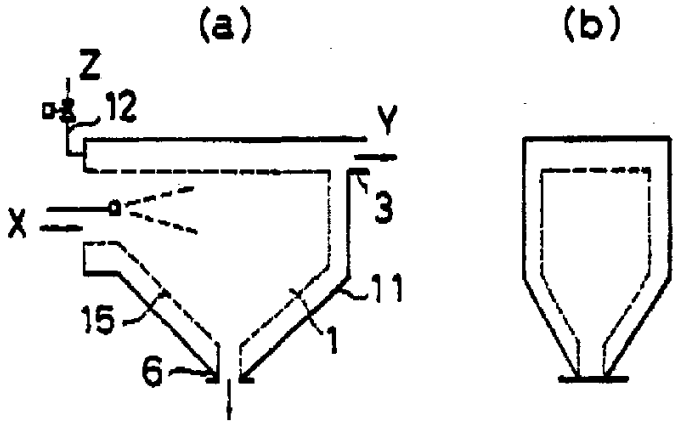


FIG. 5



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FIG. 6

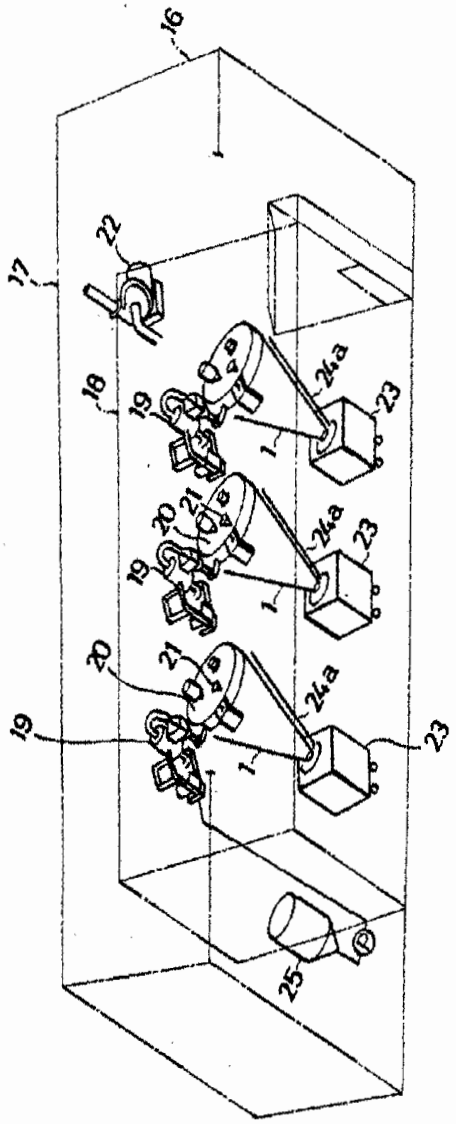
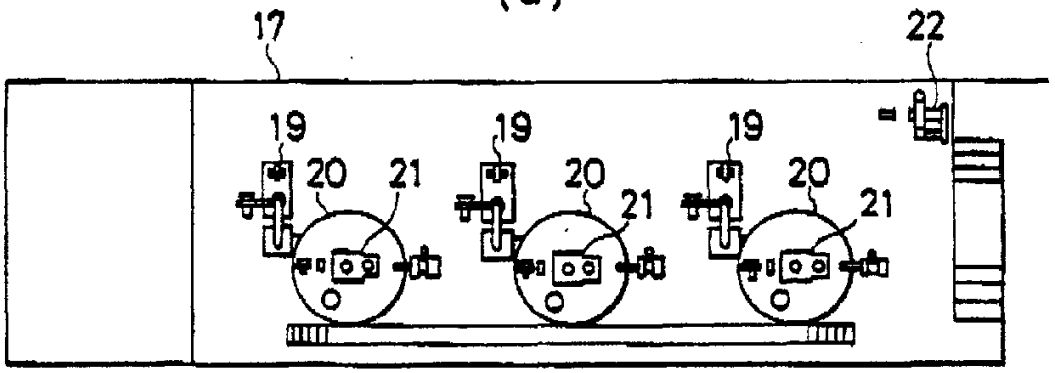
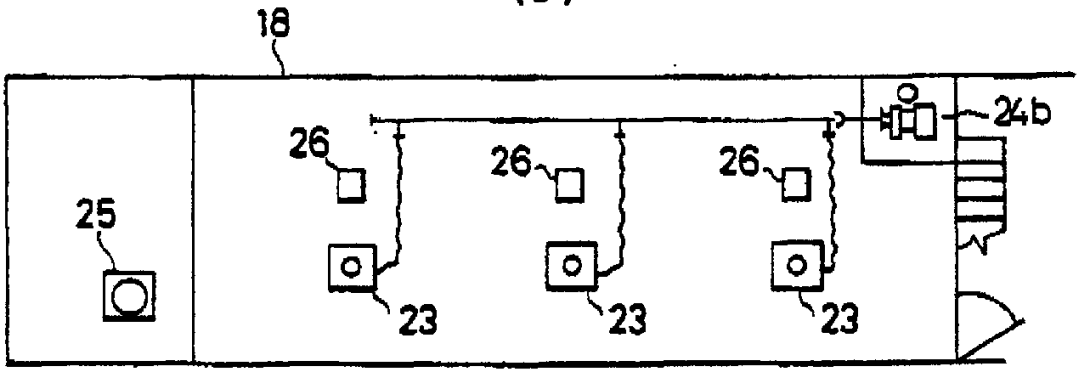


FIG. 7

(a)

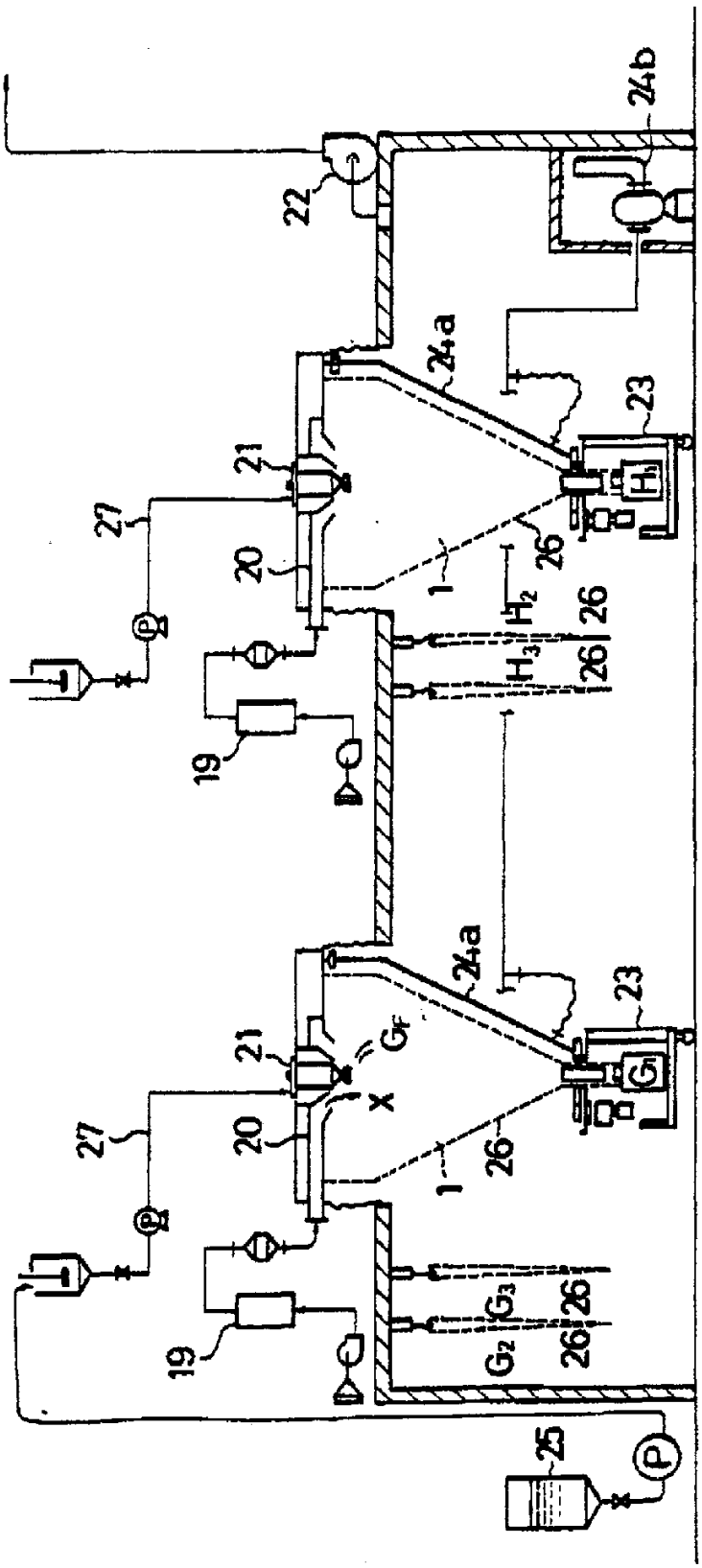


(b)



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FIG. 8



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FIG. 9

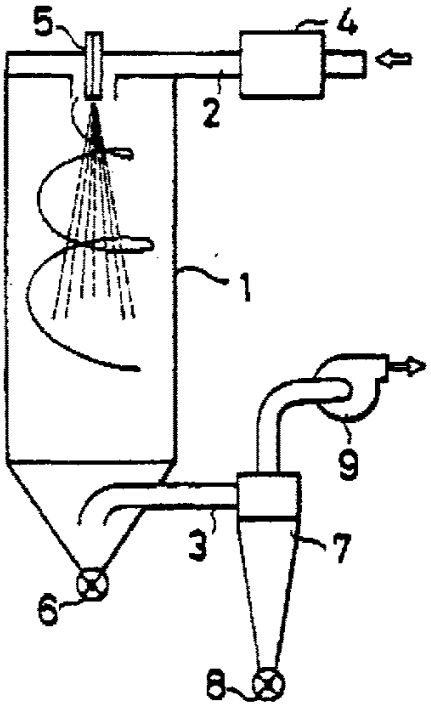
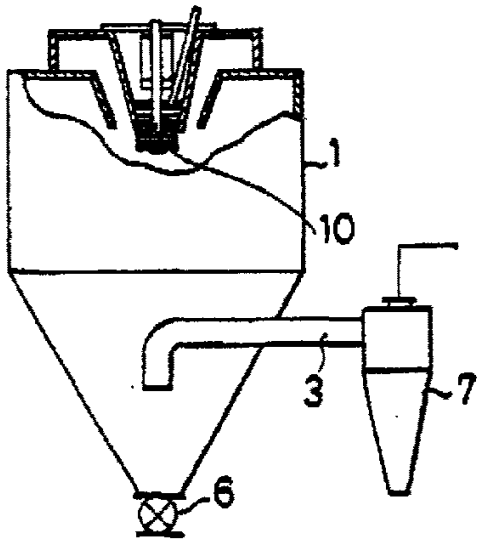


FIG. 10



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(54) **ENERGY CONSERVING PROCESS FOR DRYING A CLAY SLURRY.**

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US-A-4 222 981
US-A-4 246 039
US-A-4 312 761
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EP 0 232 313 B1

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Courier Press, Leamington Spa, England.

Description

Background of the Invention

The present invention relates generally to the processing of clay and, more particularly, to an improved method for concentrating a beneficiated aqueous kaolin clay slurry which includes evaporating water therefrom through spray drying wherein at least a portion of the energy expended in evaporating water from the slurry is recovered and used in the clay processing.

Kaolin clay has many known applications in industry, including use as a filler in papermaking, a coating for paper, and a pigment in paint. However, crude kaolin clay typically contains various impurities which cause discoloration. Additionally, crude kaolin is typically too abrasive for direct use in these products. Therefore, it is necessary to beneficiate the crude kaolin clay by various well-known commercial processes which increase the brightness of the kaolin by removing discoloration impurities and decrease the abrasiveness by reducing the particle size of the kaolin particles.

In general, such processes for beneficiating crude kaolin clay require that the clay be processed as a low solids slurry. Therefore, it is necessary to add substantial amounts of water to the dry crude kaolin clay to form a clay suspension or slurry having a low solids content, typically in the range of 15% to 40% by weight. However, for commercial applications, the beneficiated clay slurry must have a much higher solids content. Typically, beneficiated kaolin clays are shipped commercially for use in paper making, paper coating and paint making as a high solids slurry having a solids content in the range of 65% to 75% by weight. Therefore, most of the water added to the dry kaolin clay must be removed in order to concentrate the clay solids.

To dewater a beneficiated clay slurry, the low-solids slurry is typically first passed to a vacuum or press type filter wherein a limited portion of the water is removed from the slurry. Typically, the filter cake from the filter would have a solids content of about 50% to 60% by weight. Thus, the slurry would still comprise about 40% to 50% water. Further dewatering on a vacuum or press type filter is impractical due to the fine particle size of the solids in the beneficiated clay slurry. Typically, to further dewater the beneficiated clay slurry to a commercially acceptable solids content, at least a portion of the partially dewatered slurry is passed through a spray dryer or other direct contact-type evaporator such as a gas-fired kiln, wherein the clay slurry is contacted with a drying medium having a temperature of 538°C (1000°F) or more, such as hot air or hot flue gas typically generated from the combustion of natural gas. Although all of the clay slurry may be passed through the spray dryer for drying, it is customary to pass only a portion of the clay slurry through the spray dryer and then to re-mix the thoroughly dried clay slurry from the spray dryer with the remaining portion of partially dewatered slurry in a high shear mixer to produce a product clay slurry having a solids content of 65% to 75%.

A problem associated with concentrating clay slurries in spray dryers is that spray drying is a relatively inefficient process and considerable energy must be consumed in the spray drying process in order to evaporate the water in the clay slurry. In prior art spray drying systems used for concentrating clay slurries, the water vapor evaporated from the clay slurry in the drying process is typically merely vented directly to the atmosphere in the exhaust gas from the dryer as shown in US-A-4,246,039 of Mixon, or condensed but without heat recovery. For example, in US-A-4,222,981, Caswell disclosed a process for drying a clay slurry via pre-filtration and evaporative drying wherein the exhaust gases from the spray dryer are condensed via indirect heat exchange with a cooling liquid to permit recovery of organic liquids in the exhaust gases. In US-A-4,171,243, Brooks' disclose contacting the exhaust gases from an aqueous slurry spray dryer with a scrubbing solution to remove liquid and solid contaminants from the exhaust gases prior to venting the scrubbed gases to the atmosphere.

Additionally, US-A-4,473,438 of Loureiro for the spray drying of aqueous solid containing liquids wherein the exhaust gases from the spray dryer are passed to a spray tower and contacted with water to adiabatically cool the gases and increase the water content of the gases. A first portion of the cooled, humidified gases are heated in a furnace and recycled to the spray dryer, while a second portion of the cooled, humidified gases are condensed via indirect heat exchange with a cooling liquid to form a condensate which may be passed in heat exchange relationship with air being supplied to the furnace so as to preheat the air.

None of these prior art systems discloses or even suggests recovering a substantial portion of the energy expended in evaporating water from the aqueous slurry by directly contacting the exhaust gases from the dryer with a cooling liquid to form a condensate which is used to preheat the aqueous clay slurry being processed.

It is therefore a general object of the present invention to provide an improved method for concentrating a beneficiated aqueous clay slurry via spray drying in an energy efficient manner wherein the energy expended in evaporating water from the clay slurry is at least in part recovered and used in the clay slurry processing.

Summary of the Invention

The solids content of an aqueous clay slurry is concentrated by evaporating water therefrom by passing the aqueous clay slurry in contact with a hot drying gas in an evaporative dryer. Energy, normally wasted when the water vapor evaporated from the clay during the drying is vented to the atmosphere with the exhaust gas from the dryer, is recovered by condensing at least a portion of the water vapor in the exhaust gas prior to venting the exhaust gas to the atmosphere. The

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condensate from the cooling tower is used as a heat source in the process in at least one of three ways to recover at least a portion of the heat expended in evaporating the water from the aqueous clay slurry in the evaporative dryer.

In the process of the present invention, the aqueous clay slurry is partially dewatered by filtration to remove a first portion of water therefrom which is collected as the filtrate. At least a portion of the partially dewatered clay slurry is then contacted with a hot drying gas in an evaporative dryer to remove an additional portion of water therefrom which is entrained as water vapor in the drying gas exhausted from the dryer. Prior to venting to the atmosphere, the drying gas exhausted from the dryer is then passed through a cooling tower in heat exchange relationship with a cooling liquid to cause at least a portion of the water vapor evaporated from the aqueous clay slurry to condense.

In the preferred closed-loop process of the present invention, the water vapor is condensed in the cooling tower by contacting the drying gas exhausted from the dryer with an aqueous cooling liquid. The condensate is collected and split into three portions. A first portion of the condensate is passed in heat exchange relationship with the aqueous clay slurry passing to the filtration step so as to preheat the clay slurry prior to filtration, a second portion of the condensate is passed in heat exchange relationship with the partially dewatered clay slurry passing from the filtration step so as to preheat the partially dewatered clay slurry prior to evaporative drying, and a third portion of the condensate is passed in heat exchange relationship with ambient drying gas so as to preheat the drying gas being supplied to the spray dryer. The cooled condensate is then recycled to the cooling tower to serve as cooling liquid for contacting with the drying gas exhausted from the evaporative dryer.

Additionally, it is preferred that at least a portion of the heat in the filtrate from the filtration step be recovered by passing the filtrate in heat exchange relationship with ambient aqueous clay slurry from the beneficiation process to preheat the aqueous clay slurry prior to concentrating the solids therein.

Brief Description of the Drawings

The sole figure of drawing is a schematic view of a preferred embodiment of the process of the present invention using a closed-loop heat recovery system.

Description of the Preferred Embodiment

In order to be useful for paper filling, paper coating, paint making and other industrial purposes, naturally occurring kaolin crude clays must generally be processed to upgrade the clay in brightness and to reduce abrasiveness of the clay. In conventional processing for producing beneficiating kaolin clay, the crude kaolin clay is first plunged in water with a dispersing agent to form a clay-in-water suspension or slurry. After degritting and fractionation on a centrifuge to recover a desired particle size fraction, the fine particle fraction is typically diluted with water of 15% to 40% by weight solids content. This suspension is then typically treated with a bleaching compound containing a reducing agent, such as the dithionite ion, to reduce ferric ions in the clay to the ferrous state. After allowing the clay fraction to react with the reducing agent for a period of time, the clay fraction is then filtered, rinsed and then dried to concentrate the solids content of the clay for shipment. For most commercial purposes, the clay slurry is shipped at a solids content of at least 65% by weight, and typically in the range of about 70% to about 75% solids by weight. However, in some instances, the beneficiated clay is shipped as a substantially dry powder having a water content of less than about 1% by weight.

The process of the present invention, as illustrated in the preferred embodiment utilizing a closed-loop heat recovery cycle, provides an improved process for concentrating the solids in such a beneficiated clay slurry for shipment by evaporating water therefrom by passing the aqueous clay slurry first through a filter apparatus and then through an evaporative dryer. Energy expended in evaporating the water from the slurry in the evaporative dryer was typically wasted in the prior art when the water vapor evaporated from the clay during the evaporative drying process was vented to the atmosphere with the exhaust gas from the dryer. In the process of the present invention, this energy is recovered by condensing at least a portion of the water vapor in the dryer exhaust gas prior to venting the exhaust gas to the atmosphere. The recovered condensate is then utilized in the processing of the clay slurry whereby at least a portion of the energy expended in evaporating the water from the aqueous clay slurry is recovered.

Referring now to the drawing, the beneficiated low-solids aqueous kaolin slurry is passed to a filter apparatus 10, such as a rotary vacuum filter or a press filter, wherein the aqueous kaolin clay slurry is partially dewatered from a solids content typically in the range of 15% to 40% solids by weight to a solids content of about 50% to 60% by weight. Further dewatering on a rotary vacuum filter or press-type filter is impractical due to the fine particle size of the solids in the beneficiated clay slurry. Therefore, the partially dewatered kaolin clay slurry is passed to the evaporative dryer 20, which is shown in the drawing as a typical commercially available spray dryer, although other evaporative dryers of the type wherein the slurry to be dried is directly contacted with a hot drying gas, whereby water is evaporated from the slurry and entrained in the drying gas, may be used in carrying out the process of the present invention. In the spray dryer 20, a spray of the aqueous clay slurry 9 is contacted with a hot drying gas 25 whereby an additional portion of the water in the aqueous clay slurry 9 is

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removed therefrom by evaporation and entrained as water vapor in the drying gas 27 exhausted from the spray dryer 20. The product clay 11 collecting in the bottom of the spray dryer has been thoroughly dried to a water content typically of less than about 1% by weight. The thoroughly dry product clay 11 may be shipped as a dry powder if desired, but typically for most commercial uses it is remixed with a portion 13 of the 50% to 60% solids clay slurry from the filter apparatus 10 to produce a higher solids clay slurry for shipment, typically at a solids content in the range of 65% to 75% by weight.

In the process of the present invention, the drying gas exhaust 27 from the evaporative spray dryer 20 is passed in heat exchange relationship with a cooling liquid in a condensing cooling tower 40 to recover in the condensate at least a portion of the heat energy expended in evaporating the water from the aqueous clay slurry. In the preferred closed-loop embodiment, the drying gas 27 exhausted from the spray dryer 20 is contacted with a spray 59 of an aqueous cooling liquid which causes at least a portion of the water vapor entrained in the drying gas 27 exhausted from the spray dryer 20 to condense as the drying gas 27 is cooled upon contact with the cooling liquid 59. The water vapor condensing from the drying gas 27 in the cooling tower 40 collects in the bottom of the cooling tower 40 as condensate 41. The cooled drying gas 29 leaving the condensing cooling tower 40 is vented to the atmosphere.

It is to be understood that the cooling tower 40 may comprise any of a number of well known and commercially available condensing type cooling towers. In the embodiment shown in the drawing, the cooling tower 40 is a direct contact type condenser wherein a spray of aqueous cooling liquid 59 is directed into the gas stream through a plurality of spray nozzles 42 in countercurrent flow with the drying gas flowing upwardly through the cooling tower 40. Wetting surface means 44 are disposed beneath the spray nozzles 42 and are traversed by the gas flowing upwardly through the cooling tower 40. The wetting surface means 44 provides an increased surface over which the cooling liquid 59 will flow in draining to the bottom of the cooling tower 40 and come in intimate contact with the gas passing upwardly through the cooling tower 40 thereby ensuring efficient cooling of the gas. Demister means 46 are disposed above the spray nozzles 42 to remove excess moisture from the gas prior to venting the gas 29 to the atmosphere.

In accordance with the present invention, the condensate 41 collecting in the cooling tower 40 is utilized for a source of heat in the process for concentrating the solids in the aqueous clay slurry whereby at least a portion of the heat energy expended in evaporating the water from the aqueous clay slurry in the spray dryer 20 is recovered. More specifically, the condensate 41 is pumped from the cooling tower 40 in heat exchange relationship with one or more clay slips within the process so as to preheat those clay slips, or in heat exchange relationship with the drying gas being supplied to the spray dryer 20 so as to assist in the heating of the drying gas. Having been cooled during such heat exchange, the cooled condensate 41 is then passed back to the cooling tower 40 and injected through spray nozzles 42 to form at least a substantial portion of the cooling liquid spray 59 contacted with the drying gas passing through the cooling tower 40. The aqueous cooling liquid will be comprised substantially of water and for the most part water condensed from the exhaust gas, i.e. the recycled condensate 41. However, the aqueous cooling liquid may include other constituents in addition to water. For instance, if desired, an agent such as ethylene glycol or propylene glycol may be added to the water to enhance the condensation process. Additionally, a pH modifier may be added as desired to the water to adjust the pH of the condensate 41 in order to control corrosion in the heat exchangers through which the condensate will pass in the heat recovery process.

In the process of the present invention, three particular uses are contemplated for the condensate 41. These include preheating the aqueous clay slurry 7 prior to filtration in the filter means 10, preheating the partially dewatered aqueous clay slurry 9 from the filtration step prior to evaporative drying in the spray dryer 20, and preheating an ambient stream 21 of drying gas prior to passing the drying gas through the main heating means 30 and thence to the spray dryer 20. In the preferred closed-loop embodiment of the process of the present invention shown in the drawing, the condensate 41 pumped from the cooled tower 40 is split into three portions, 43, 45 and 47. The first portion 43 of the condensate 41 from the cooling tower 40 is passed through heat exchanger 50 in indirect heat exchange relationship with the aqueous clay slurry 7 passing to the filter means 10 so as to preheat the aqueous clay slurry 7 prior to filtration and to cool the first portion 43 of the condensate 41 thereby recovering at least a portion of the energy expended in evaporating water from the aqueous clay slurry in the spray dryer 20. In this manner, the clay slurry being fed to the filter means 10 is preheated preferably to a temperature of about 54°C (130°F) prior to filtration. In the process of passing in heat exchange relationship with the aqueous clay slurry 7 in the heat exchanger 50, the first portion 43 of the condensate 41 is cooled to a temperature in the range of 43°C to 49°C (110°F to 120°F). The cooled condensate 53 is then collected and recycled back to the cooling tower 40 to form a portion of the cooling water sprayed through spray nozzles 42 into the gas stream 27 passing through the cooling tower 40.

The second portion 45 of the condensate 41 from the cooling tower 40 is passed through heat exchanger 70 in indirect heat exchange relationship with the partially dewatered kaolin clay slurry 9 passing from the filtration step carried out in the filter means 10. In this manner, the partially dewatered kaolin clay slurry 9 to be sprayed into

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the spray dryer 20 to contact the hot drying gas therein is preferably preheated to a temperature in the range of about 60°C to 66°C (140°F to 150°F). This preheating of the slurry feed to the spray dryer 20 reduces the amount of heat energy which must be input to the clay slurry within the spray dryer 20 in order to bring the clay slurry up in temperature to the point where evaporation of the water therein will readily occur within the spray dryer 20. Thus, a lower quantity of hot drying gas can be input to the spray dryer 20 and still effectively evaporate water from the clay slurry 9. The second portion 45 of the condensate 41 from the spray tower 40 is cooled in passing through the heat exchanger 70 in heat exchange relationship with the partially dewatered clay slurry 9 and the cooled condensate 55, preferably to a temperature in the range of 43°C to 49°C (110°F to 120°F) and recirculated to the cooling tower 40 and injected into the exhaust gas through spray nozzles 42 to form a portion of the spray 59 of cooling liquid contacted with the exhaust gas from the spray dryer 20 within the cooling tower 40.

The third portion 47 of the condensate 41 pumped from the cooling tower 40 is passed through heat exchanger 80 in indirect heat exchange relationship with a stream of ambient air to preheat the ambient air. The preheated air 23, preferably at a temperature of about 57°C to about 63°C (about 135°F to about 145°F), is then passed to heating means 30, typically a direct-fired air heater, wherein the hot drying gases 25 to be supplied to the spray dryer 20 is generated. Generally, a fossil fuel, such as natural gas, is fired directly in the preheated air stream 23 to generate hot combustion products which form the hot drying gas 25. The hot drying gas 25 is produced in the heating means 30 and supplied to the spray dryer 20 at a temperature in the range of 538°C to 649°C (1000°F to 1200°F), and preferably about 593°C (1100°F). The third portion 47 of the condensate 41 is cooled in passing through heat exchanger 80, preferably to a temperature in the range of 43°C to 49°C (110°F to 120°F) and the cooled condensate 57 is recycled back to the cooling tower 40 and injected into the exhaust gas 27 from the spray dryer 20 through spray nozzles 42 to form a portion of the spray 59 of cooling liquid.

In the preferred embodiment of the process of the present invention shown in the drawing, further heat is recovered by passing the filtrate 71 removed from the aqueous clay slurry 7 as it passes through the filter means 10 in heat exchange relationship with the ambient aqueous clay slurry 5 being passed to the heat exchange means 50. The filtrate 71 will typically have a temperature in the range of 38°C to 45°C (100°F to 115°F) and is passed through heat exchanger 60 to pass in indirect heat exchange relationship with the ambient aqueous clay 50 which has a temperature ranging from as low as 10°C (50°F) to as high as 38°C (100°F) depending upon the season of the year. The ambient aqueous clay slurry 5 would be colder in the winter months and warmer in the summer months. By passing the aqueous clay slurry 5 in heat exchange relationship with the filtrate 71, a more uniform temperature is obtained year-round for the aqueous clay slurry 7 being passed to the first heat exchange means 50 in heat exchange relationship with the first portion 43 of the condensate 41 and then onto the filter means 10. The cooled filtrate 73 from the heat exchanger 60 is then passed to disposal and handled in a conventional manner.

It is to be understood that the process of the present invention may be carried out without splitting the condensate 41 from the cooled tower 40 into three separate streams as shown in the preferred embodiment of the present invention illustrated in the drawing. Depending on the particular circumstances of any given process, it may be desirable to split the condensate 41 into only two streams and to use those two streams to perform only two of the preheat functions discussed hereinbefore, or to leave the condensate stream as a whole and perform only one of those preheat functions, or even to use a single stream of condensate 41 to perform two or more of the heat exchange functions in series. The particular embodiment chosen for any application will depend upon the particular economies of the process in question.

Furthermore, it is contemplated that even in the preferred closed-loop three stream embodiment of the process of the present invention illustrated in the drawing, that the distribution of the condensate 41 between the three streams 43, 45 and 47 will vary from one application to another with the distribution of the three streams by no means constrained to be an equal distribution thereamongst. In fact, it is contemplated that in most applications the stream 45 used to preheat the partially dewatered aqueous clay slurry passing from the filtration step to the evaporative dryer will constitute the greatest portion of the condensate as this appears to be the most efficient use of the heat contained in the condensate. The optimum number of streams into which the condensate 41 is to be split and the particular distribution amongst those streams will vary with the economics of each application of the process of the present invention.

Claims

1. A process for concentrating solids in an aqueous clay slurry comprising: dewatering the aqueous clay slurry by filtration to remove a first portion of water therefrom and collecting the water removed from the aqueous clay slurry as the filtrate from said filtration step; contacting the partially dewatered aqueous clay slurry from said filtration step with a hot drying gas in an evaporative dryer whereby an additional portion of the water in the aqueous clay slurry is removed therefrom by evaporation; and condensing at least a portion of the water vapor in the drying gas exhausted from the evaporative dryer by

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passing the drying gas in heat exchange relationship with a cooling liquid in a cooling tower, said process characterized by the further step of passing at least a portion of the condensate from the cooling tower in heat exchange relationship with the aqueous clay slurry being processed thereby cooling the condensate and recovering at least a portion of the energy expended in evaporating the water from the aqueous clay slurry in the evaporative dryer.

2. A process as recited in Claim 1, characterized by preheating the aqueous clay slurry prior to filtration by passing at least a portion of the condensate from the cooling tower in heat exchange relationship with the aqueous clay slurry passing to said filtration step.

3. A process as recited in Claim 2 further characterized by recycling the cooled condensate having passed in heat exchange relationship with the aqueous clay slurry passing to said filtration step to the cooling tower to form at least a portion of the spray of cooling liquid contacted with the drying gas exhausted from the evaporative dryer.

4. A process as recited in Claim 3 further characterized by passing the filtrate from said filtration step in heat exchange relationship with the aqueous clay slurry prior to passing the aqueous clay slurry in heat exchange relationship with the first portion of the condensate from the cooling tower.

5. A process as recited in Claim 2 further characterized in the aqueous clay slurry is preheated prior to said filtration step to a temperature of about 54°C (130°F).

6. A process as recited in Claim 1 characterized by preheating the partially dewatered aqueous clay slurry from said filtration step prior to evaporative drying by passing at least a portion of the condensate from the cooling tower in heat exchange relationship with the partially dewatered clay slurry passing from said filtration step.

7. A process as recited in Claim 6 further characterized by recycling the cooled condensate having passed in heat exchange relationship with the partially dewatered aqueous clay slurry passing from said filtration step to the cooling tower to form at least a portion of the spray of cooling liquid contacted with the drying gas exhausted from the evaporative dryer.

8. A process as recited in Claim 6 further characterized in that the partially dewatered clay slurry from said filtration step is heated prior to evaporative drying to a temperature in the range of about 57°C (135°F) to about 63°C (145°F).

9. A process as recited in Claim 1 characterized by passing at least a portion of the condensate from the cooling tower in heat exchange relationship with an ambient stream of drying gas to preheat the stream of drying gas.

10. A process as recited in Claim 9 further characterized by recycling the cooled condensate having passed in heat exchange relationship with the ambient stream of drying gas to the cooling tower to form at least a portion of the spray of cooling liquid contacted with the drying gas exhausted from the evaporative dryer.

11. A process as recited in Claim 1 characterized by recovering a portion of the energy expended in evaporating the water from the aqueous clay slurry in the evaporative dryer by:

a. passing a first portion of the condensate from the cooling tower in heat exchange relationship with the aqueous clay slurry passing to said filtration step so as to preheat the aqueous clay slurry prior to filtration;

b. passing a second portion of the condensate from the cooling tower in heat exchange relationship with the partially dewatered clay slurry passing from said filtration step so as to preheat the partially dewatered clay slurry prior to evaporative drying; and

c. passing a third portion of the condensate from the cooling tower in heat exchange relationship with the drying gas so as to partially heat the drying gas prior to contacting the partially dewatered clay slurry with the drying gas in the evaporative dryer.

Patentansprüche

1. Verfahren zur Feststoffkonzentrierung in wäßrigem Tonschlamm bestehend aus den Schritten: Entwässerung des wäßrigen Tonschlamms durch Filtration zur Entfernung eines ersten Teils Wassers sowie Sammlung des vom wäßrigen Tonschlamm entfernten Wassers als Filtrat jener Filtrationsstufe; Behandlung des teilweise entwässerten wäßrigen Tonschlamms aus jener Filtrationsstufe mit heißem Trockengas in einem Verdampfungstrockner, wobei ein weiterer Teil des Wassers aus dem wäßrigen Tonschlamm durch Verdampfung entfernt wird; sowie Kondensation zumindest eines Teils des Wasserdampfes in dem vom Verdampfungstrockner ausgestoßenen Trockengas durch Wärmeaustausch mittels einer Kühlflüssigkeit in einem Kühlturm, dadurch gekennzeichnet, daß ein weiterer Schritt dieses Verfahren darin besteht, daß man zumindest einen Teil des Kondensats aus dem Kühlturm einem Wärmeaustausch mit dem aufzubereitenden wäßrigen Tonschlamm unterzieht, wodurch man das Kondensat kühlt und zumindest einen Teil der zur Verdampfung des Wassers aus dem wäßrigen Tonschlamm in dem Verdampfungstrockner verbrauchten Energie wieder-gewinnt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man den wäßrigen Tonschlamm vor der Filtration durch Wärmeaustausch zumindest eines Teils des Kondensats aus dem Kühlturm mit dem, jener Filtrationsstufe zuzuführenden, wäßrigen Tonschlamm erhitzt.

3. Verfahren nach Anspruch 2, weiterhin dadurch gekennzeichnet, daß man das gekühlte Kondensat nach dem Wärmeaustausch mit dem jener Filtrationsstufe zuzuführenden, wäßrigen Tonschlamm in den Kühlturm zurückführt, damit zumindest ein Teil der mit dem vom Verdampfungstrockner ausgestoßenen Trockengas zu

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behandelnden Sprühkühlflüssigkeit gebildet wird.

4. Verfahren nach Anspruch 3, weiterhin dadurch gekennzeichnet, daß man das Filtrat aus jener Filtrationsstufe einem Wärmeaustausch mit dem wäßrigen Tonschlamm unterzieht, bevor man den wäßrigen Tonschlamm einem Wärmeaustausch mit dem ersten Teil des Kondensats aus der Kühlturm unterzieht.

5. Verfahren nach Anspruch 2, weiterhin dadurch gekennzeichnet, daß man den wäßrigen Tonschlamm vor jener Filtrationsstufe auf eine Temperatur von ungefähr 54°C (130°F) erhitzt.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man den teilweise entwässerten wäßrigen Tonschlamm aus jener Filtrationsstufe vor dem Verdampfungstrocknen dadurch erhitzt, daß man zumindest einen Teil des Kondensats aus dem Kühlturm einem Wärmeaustausch mit dem teilweise entwässerten, von der Filtrationsstufe stammenden Tonschlamm unterzieht.

7. Verfahren nach Anspruch 6, weiterhin dadurch gekennzeichnet, daß man das gekühlte Kondensat nach dem Wärmeaustausch mit dem teilweise entwässerten, aus besagter Filtrationsstufe stammenden, wäßrigen Tonschlamm in den Kühlturm zurückführt, damit zumindest ein Teil der mit dem vom Verdampfungstrockner ausgestoßenen Trockengas zu behandelnden Sprühkühlflüssigkeit gebildet wird.

8. Verfahren nach Anspruch 6, weiterhin dadurch gekennzeichnet, daß man den teilweise entwässerten Tonschlamm aus jener Filtrationsstufe vor dem Verdampfungstrocknen auf eine Temperatur im Bereich von ungefähr 57°C (135°C) bis etwa 63°C (145°C) erhitzt.

9. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man zumindest einen Teil des Kondensat aus dem Kühlturm einem Wärmeaustausch mit einem umgebenden Trockengasstrom zwecks Vorerhitzen des Trockengasstroms unterzieht.

10. Verfahren nach Anspruch 9, weiterhin dadurch gekennzeichnet, daß man das gekühlte Kondensat nach dem Wärmeaustausch mit dem ungebenden Trockengasstrom in den Kühlturm zurückführt, damit zumindest ein Teil der mit dem vom Verdampfungstrockner ausgestoßenen Trockengas zu behandelnden Sprühkühlflüssigkeit gebildet wird.

11. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man ein Teil der zum Verdampfen des Wassers aus dem wäßrigen Tonschlamm in dem Verdampfungstrockner verbrauchten Energie dadurch wiedergewinnt, daß man:

a. einen ersten Teil des Kondensats aus dem Kühlturm einem Wärmeaustausch mit dem jenes Filtrationsstufe zuzuführenden, wäßrigen Tonschlamm unterzieht, damit der wäßrige Tonschlamm vor der Filtration erhitzt wird;

b. einen zweiten Teil des Kondensats aus dem Kühlturm einem Wärmeaustausch mit dem aus jener Filtrationsstufe stammenden, teilweise entwässerten Tonschlamm unterzieht, damit der teilweise entwässerte Tonschlamm vor dem Verdampfungstrocknen erhitzt wird; und

c. einen dritten Teil des Kondensats aus dem Kühlturm einem Wärmeaustausch mit dem Trokkengas unterzieht, damit das Trockengas vor der Behandlung dem teilweise entwässerten Tonschlamms mit dem Trockengas in dem Verdampfungstrockner teilweise erhitzt wird.

Revendications

1. Procédé de concentration des solides dans une boue d'argile aqueuse, comprenant: l'essorage de la boue d'argile aqueuse par filtrage pour enlever une première portion de l'eau de celle-ci et la collecte de l'eau enlevée de la boue d'argile aqueuse sous forme de filtrat dudit filtrage; la mise en contact de la boue d'argile aqueuse partiellement essorée provenant de ladite étape de filtrage avec un gaz de séchage chaud dans un séchoir à évaporation, ce qui permet d'enlever de la boue d'argile aqueuse une portion supplémentaire d'eau par évaporation; et la condensation d'au moins une portion de la vapeur d'eau du gaz de séchage évacué du séchoir à évaporation en faisant circuler le gaz de séchage en échange de chaleur avec un liquide de refroidissement dans une tour de refroidissement, ledit procédé étant caractérisé par l'étape supplémentaire consistant à faire passer au moins une portion du condensat de la tour de refroidissement en échange de chaleur avec la boue d'argile aqueuse traitée, refroidissant ainsi le condensat et récupérant au moins une portion de l'énergie consommée pour évaporer l'eau de la boue d'argile aqueuse dans le séchoir à évaporation.

2. Procédé suivant la revendication 1, caractérisé en ce que l'on préchauffe la boue d'argile aqueuse avant le filtrage en faisant passer au moins une portion du condensat de la tour de refroidissement en échange de chaleur avec la boue d'argile aqueuse circulant vers ladite étape de filtrage.

3. Procédé suivant la revendication 2, caractérisé en outre en ce que l'on recycle le condensat refroidi, qui est passé en échange de chaleur avec la boue d'argile aqueuse circulant vers ladite étape de filtrage, à la tour de refroidissement pour former au moins une partie du jet pulvérisé de liquide de refroidissement mis en contact avec le gaz de séchage provenant du séchoir à évaporation.

4. Procédé suivant la revendication 3, caractérisé en outre en ce que l'on fait passer le filtrat provenant de ladite étape de filtrage en échange de chaleur avec la boue d'argile aqueuse avant de faire passer la boue d'argile aqueuse en échange de chaleur avec la première portion du condensat de la tour de refroidissement.

5. Procédé suivant la revendication 2, caractérisé en ce que la boue d'argile aqueuse est préchauffée avant ladite étape de filtrage jusqu'à une température d'environ 54°C (130°F).

6. Procédé suivant la revendication 1, caractérisé en ce que l'on préchauffe la boue d'argile aqueuse partiellement essorée provenant de

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ladite étape de filtrage avant le séchage par évaporation en faisant passer au moins une portion du condensat de la tour de refroidissement en échange de chaleur avec la boue d'argile partiellement essorée provenant de ladite étape de filtrage.

7. Procédé suivant la revendication 6, caractérisé en outre en ce que l'on recycle le condensat refroidi, qui est passé en échange de chaleur avec la boue d'argile aqueuse partiellement essorée provenant de ladite étape de filtrage, à la tour de refroidissement pour former au moins une partie du jet pulvérisé de liquide de refroidissement mis en contact avec le gaz de séchage évacué du séchoir à évaporation.

8. Procédé suivant la revendication 6, caractérisé en outre en ce que la boue d'argile partiellement essorée provenant de ladite étape de filtrage est chauffée avant le séchage par évaporation jusqu'à une température comprise entre environ 57°C (135°F) et environ 63°C (145°F).

9. Procédé suivant la revendication 1, caractérisé en ce que l'on fait passer au moins une portion du condensat de la tour de refroidissement en échange de chaleur avec un courant ambiant de gaz de séchage pour préchauffer le courant de gaz de séchage.

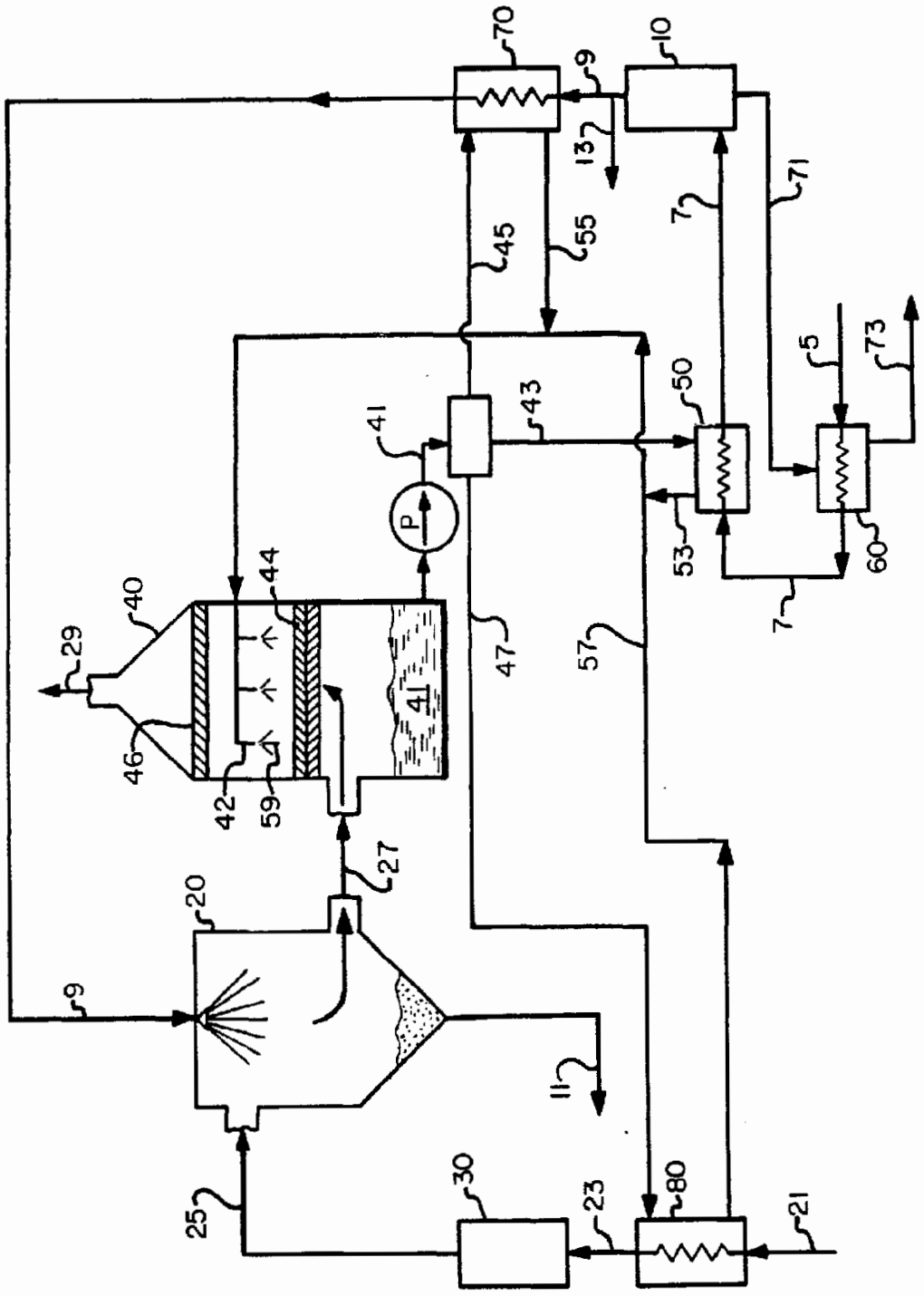
10. Procédé suivant la revendication 9, caractérisé en outre en ce que l'on recycle le condensat refroidi, qui est passé en échange de chaleur avec le courant ambiant de gaz de séchage, à la tour de refroidissement pour former au moins une partie du jet pulvérisé de liquide de refroidissement mis en contact avec le gaz de séchage évacué du séchoir à évaporation.

11. Procédé suivant la revendication 1 caractérisé en ce que l'on récupère une portion de l'énergie consommée pour évaporer l'eau de la boue d'argile aqueuse dans le séchoir à évaporation, en:

a. faisant passer une première portion du condensat de la tour de refroidissement en échange de chaleur avec la boue d'argile aqueuse circulant vers ladite étape de filtrage, de façon à préchauffer la boue d'argile aqueuse avant le filtrage; en

b. faisant passer une deuxième portion du condensat de la tour de refroidissement en échange de chaleur avec la boue d'argile partiellement essorée provenant de ladite étape de filtrage, de façon à préchauffer la boue d'argile partiellement essorée avant le séchage par évaporation; et en

c. faisant passer une troisième portion du condensat de la tour de refroidissement en échange de chaleur avec le gaz de séchage, de façon à chauffer partiellement le gaz de séchage avant de mettre la boue d'argile partiellement essorée en contact avec le gaz de séchage dans le séchoir à évaporation.


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(54) Spray dried ibuprofen.

(57) A therapeutic taste-neutral powder form of ibuprofen obtained by spray-drying a dispersion of ibuprofen and ethyl cellulose in water having a plasticiser dissolved or suspended therein.

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SPRAY DRIED IBUPROFEN

This invention relates to a novel therapeutic form of spray dried ibuprofen having a neutral taste which can be formulated into, for example, chewable tablets and fast dissolving dosage forms as described in United States Letters Patent Nos. 4,305,502 and 4,371,516. More specifically this invention relates to a taste neutral spray dried powder formed by spray drying a dispersion of ibuprofen and ethylcellulose in water having a plasticizer dissolved or suspended therein. By taste-neutral it is meant that the powder has essentially no taste and is not sweet nor bitter.

Ibuprofen, a widely used analgesic and antipyretic, is not palatable enough to be used in chew-type tablets for those people who do not swallow whole solid-type dosage forms.

The use of flavour agents eg. chocolate, banana, orange, lemon, licorice, root beer, and raspberry, in particular, have been proposed for bitter tasting drugs. These agents are not dependable masking ingredients. Mint flavours can be useful in ameliorating a chalky taste parameter. Bitter properties, however, are very difficult to mask to any great extent, particularly, when they do not mimic the expected natural taste of the flavour agent.

Other properties including mouthfeel also need to be addressed in consideration of the oral acceptance of chewable or chew-type tablets.

The fast dissolving dosage forms described in United States Letters Patent Nos. 4,305,502 and 4,371,516 are manufactured to disintegrate in water within ten seconds or less and hence dissolve rapidly in the saliva of the mouth. Heretofore the use of such dosage forms was restricted to pharmaceuticals which had a neutral taste or a slightly disagreeable taste which could be masked by a flavouring agent. Pharmaceuticals with a bitter taste such as acetaminophen and ibuprofen, however, could not heretofore be used in such dosage forms.

According to this invention, a novel therapeutic taste-neutral powder form of spray-dried ibuprofen is provided which can be formulated into chewable tablets and the like. The powder is formed by spray drying a dispersion of ibuprofen and ethyl cellulose in water having a plasticizer dissolved or suspended therein. Preferably a small amount of a suspending agent to suspend the ibuprofen in the dispersion is employed.

According to another aspect of this invention, a pharmaceutical dosage form for oral administration as a solid is provided, which dosage form can be disintegrated by water at 37° C within ten seconds, and comprises as the pharmaceutical agent incorporated therein the taste neutral powder form of spray dried ibuprofen of this invention.

The ibuprofen useful in this invention is the pharmaceutical grade in finely powdered or micronized form. The ethyl cellulose useful in this invention is also National Formulary or pharmaceutical grade.

Suitable grades are the AQUACOAT brand marketed by FMC Corporation of Newark, Delaware and the SURELEASE brand marketed by Colorcon Incorporated, West Point, Pennsylvania.

The plasticizers useful in this invention include dibutyl sebacate, glycerin, propylene glycol, triacetin, triethyl citrate, and low molecular weight polyethylene glycols such as CARBOWAX 600, marketed by UNION CARBIDE CORP. of Danbury, Connecticut. A suitable plasticizer is UNIFLEX brand of dibutyl sebacate marketed by Union Camp Corp. of Jacksonville, Florida.

The suspending agents to suspend the ibuprofen in the dispersion prior to spray drying can be of the usual type such as microcrystalline cellulose polyvinylpyrrolidone, and the like. The weight percent of ibuprofen in the taste neutral powder can be from about 63% to 77% by weight, preferably 63% to 73%, and the weight percent of the ethylcellulose can range from about 25% to 40%, preferably about 28% to 40% by weight, more preferably 25% to 35%. At about 25% by weight of ethylcellulose, there is no bitter taste and the powder is taste neutral. The weight percent of plasticizer in the taste neutral powder can be from about 2% to 7% by weight.

Spray dryers can be of the usual laboratory or commercial type. Suitable spray dryers are manufactured by Buchi Laboratorismus-Technik AG., by the Anydro Company of Attleboro, Massachusetts and by Niro Atomizer Inc., of Columbia, Maryland. The spray dryer employed in the following examples was a Niro Portable Spray Dryer, Model No. 21231-0001. The operating conditions include a variable air inlet temperature, a variable outlet temperature, a variable air pressure of compressed air driving the atomizer wheel, and a variable feed rate.

The following examples illustrate the formation of the taste-neutral spray dried ibuprofen powder of the invention. In these examples, the ibuprofen was obtained from Ethyl Corporation, Baton Rouge, Louisiana, and the ethyl cellulose was obtained from FMC Corporation, Newark, Delaware as AQUACOAT. It was a 30% solids dispersion in water of the standard type having an ethoxy content of 48.0% to 49.5%.

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EXAMPLE I

In this example, the feed mixture to the spray dryer was composed of the following materials.

Ingredient	Weight % Solids in powder	Grams Ingredient in suspension	Grams Solids in suspension
Ibuprofen, USP	74	200	200
Polyvinylpyrrolidine		0.4	0.4
AQUACOAT brand of Ethyl Cellulose,NF	22	200	60
Uniflex brand of Dibutyl Sebacate	4	12	12
Deionized Water	---	1100	---
Total:	100%	1512.4grams	272.4

Approximately 200 grams of finely divided ibuprofen were passed through a 20 mesh (Tyler) screen and 200 grams of the screened ibuprofen were retained. The 1200 grams of deionized water were placed in a stainless steel mixing vessel equipped with a Lightnin mixer. With mixing and slowly added to the water were the polyvinylpyrrolidone and the ibuprofen powder. Mixing was continued for 30 minutes. In a separate stainless steel mixing vessel equipped with a Lightnin mixer the dibutyl sebacate was mixed with the AQUACOAT brand of ethyl cellulose for 30 minutes. The ethyl cellulose-dibutyl sebacate mixture was then added to the ibuprofen suspension and mixed for 30 minutes. The dispersion was then transferred to the feed hopper of the Niro Portable Spray Dryer.

The spray dryer was operated such that an air outlet temperature of approximately 37° C-39° C and a spray rate of 32-35 ml/minute were maintained throughout the run.

The spray dried powder with the 22% ethyl cellulose coat had a slightly bitter taste. The moisture content of the powder was 0.36-0.50%.

EXAMPLE II

In this example, the feed mixture to the spray dryer was composed of the following materials.

Ingredient	Weight % Solids in powder	Grams Ingredient in suspension	Grams Solids in suspension
Ibuprofen, USP	70.92	100	100
AQUACOAT brand of Ethyl Cellulose,NF	21.28	100	30
Uniflex brand of Dibutyl Sebacate	4.26	6	6
Microcrystalline Cellulose	3.54	5	5
Deionized Water	---	494	---
Total:	100%	705grams	141

To the 100 grams of AQUACOAT brand of ethyl cellulose as a 30% solids dispersion in water contained in a mixing vessel equipped with a Lightnin mixer were added the 6 grams of dibutyl sebacate and the dispersion was mixed for 30 minutes. The 100 grams of ibuprofen prescreened through 20 mesh (Tyler) were added to 494 grams of deionized water contained in a separate mixing vessel equipped with a Lightnin mixer to which the microcrystalline cellulose had previously been added. The ethyl cellulose-dibutyl sebacate dispersion was then mixed with the ibuprofen suspension for 30 minutes. The microcrystalline cellulose was added to the ibuprofen suspension to aid in maintaining the ibuprofen in suspension so that it does not settle out in the spray drier feed hopper. The dispersion was then transferred to the feed hopper of the Niro Portable Spray Dryer. The operating conditions for the spray drier were the same as in Example I.

The spray dried powder had a slightly bitter taste indicating that more ethyl cellulose was required to achieve a taste neutral product.

EXAMPLE III

In this example, the feed mixture to the spray dryer was composed of the following materials.

Ingredient	Weight % Solids in powder	Grams Ingredient suspension	Grams Solids in suspension
Ibuprofen, USP	66.36	100.0	100.0
AQUACOAT brand of Ethyl Cellulose,NF	26.54	133.3	40.0
Citroflex-2 brand of triethyl citrate	5.31	8.0	8.0
Microcrystalline Cellulose	1.66	2.5	2.5
Polyvinylpyrrolidone	0.15	0.225	0.225
Deionized Water	---	760.8	---
Total:	100.02	1004.825	150.725

To the 133.3 grams of AQUACOAT brand of ethyl cellulose as a 30% solids dispersion in water contained in a mixing vessel equipped with a Lightnin mixer were added the 8 grams of Citroflex-2 and the dispersion was mixed for 30 minutes. The 100 grams of ibuprofen prescreened through 20 mesh (Tyler) were added to the 760.8 grams of water to which the microcrystalline cellulose and polyvinylpyrrolidone had previously been added and mixed. The ethyl cellulose dispersion was added to the ibuprofen suspension and mixed for 30 minutes until a homogenous suspension is formed. The dispersion was then transferred to the feed hopper of the Niro Portable Spray Dryer.

The spray dryer was operated such that the air inlet temperature was about 80° C and an air outlet temperature of 37°-39° C was maintained during the run. The feed rate to the spray nozzle was about 32-35 ml/minute.

The spray dried powder had a moisture content of 0.5% and was taste neutral. After several seconds it produced a slightly bitter sensation at the back of the mouth indicating that slightly more ethyl cellulose was required to achieve a completely satisfactory product.

EXAMPLE IV

This example describes the preparation of fast dissolving dosage forms using the spray dried taste-neutral ibuprofen of Example III and other ingredients as follows:

Ingredients	Weight% suspension	Grams Ingredients per 500 grams suspension
Gelatin, BY 19/50	4.00	20.00
Mannitol,granular	3.00	15.00
Deionized water	67.50	337.50
NUTRASWEET,NF	0.60	3.00
Anise/Juicy Fruit #669	0.75	3.75
Red FD&C #40 (1% Solution)	0.25	1.25
Sodium lauryl sulfate	1.00	5.00
Sweetness Flavour # 284	0.10	0.50
Powder, Example 3	22.80	114.00
Total:	100.00	500.00

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The procedure for preparing a batch of the above suspension takes place in two stages, i.e. the preparation of the gelatin base and the addition of the pharmaceutical agent.

The gelatin base is prepared by adding the gelatin to the deionized water at 30° C and mixing until the gelatin is dissolved. The solution is then cooled to 25° C and the mannitol, the sodium lauryl sulfate, the sweetener, and the flavours are separately added and dissolved.

The freeze dryer employed in this example was a Virtis 25 SRC Model Freeze Dryer. The fast dissolving dosage forms are prepared by dosing 500 milligrams of the suspension of ibuprofen into each well in the thermoformed blister tray containing 10 wells per tray. The filled trays are placed in a larger tray containing a dry ice-methanol mixture. When the suspensions in the wells are frozen, the samples are placed on the freeze dryer trays at a shelf temperature of -45° C.

When the samples have reached a temperature of -45° C, as determined by a probe in a well, the condenser is turned on and the freezer turned off. The condenser temperature is brought to between -40° and -45° C and the vacuum is turned on to between 50 and 60 millitorrs. The heater is then turned on and the shelf temperature is adjusted to 50°-55° C. The heat dry cycle lasts for 4 hours. The vacuum, the condenser and the heater are turned off and the samples removed. The wafers from each batch are removed from the wells in the trays. They are white in colour and each weighs about 165 milligrams of which about 80 milligrams is ibuprofen. The wafers from each batch when placed on the tongue exhibit a fruit flavour with a very slight bitter after taste. When placed in water at 37° C the wafers disintegrate in less than ten seconds.

EXAMPLE V

This example describes the preparation of a chewable tablet using the spray dried taste neutral ibuprofen of Example III and other ingredients as follows:

Ingredients	Weight
Powder of Example III, 70%	120.50mg
Mannitol powder, USP	120.50mg
Confectionous sugar,6X,RF	80.25mg
Magnesium stearate	2.00mg
Sorbitol q.s. to	500.00mg
Total	500.00mg

The powder of Example III contains 66.4% by weight or 80 mg of ibuprofen. The ingredients are mixed in a suitable mixer and formed into tablets. The tablets when chewed in the mouth have a neutral taste and good mouthfeel. The taste could be improved by incorporation into the tablet of suitable flavouring agents such as a mint flavouring agent.

Claims

1. A therapeutic taste neutral powder form of spray-dried ibuprofen which consists essentially of, based upon the weight of the powder, about 63% to 77% by weight ibuprofen, about 25% to 40% by weight ethyl cellulose and about 2% to 7% by weight of a plasticiser, the powder having been spray dried from a dispersion of the ibuprofen and ethyl cellulose in water having a plasticiser dissolved or suspended therein.

2. A powder as claimed in claim 1, wherein the amount of ethyl cellulose is about 28% to 40% by weight.

3. A powder as claimed in claim 1, or claim 2, wherein the plasticiser is dibutyl sebacate.

4. A powder as claimed in claim 1 or 2, wherein the plasticiser is triethyl citrate.

5. In a pharmaceutical dosage form for oral administration as a solid, which dosage form can be disintegrated by water within ten seconds, the improvement which comprises incorporationg into such dosage form as the pharmaceutical substance a therapeutic taste-neutral powder form of spray-dried ibuprofen as claimed in anyone of claims 1 to 4.

6. In a pharmaceutical dosage form for oral administration as a solid chewable taste-neutral tablet containing ibuprofen, the improvement which comprises incorporating into such tablet as the pharmaceutical substance a therapeutic taste-neutral powder form of spray-dried ibuprofen as claimed in anyone of claims 1 to 4.

Claims for the following Contracting States: ES, GR

1. A process for preparing a therapeutic taste neutral powder form of ibuprofen which comprises mixing together in a aqueous medium, about 63 to 77% by weight ibuprofen, about 25% to 40% by weight ethyl cellulose and about 2% to 7% by weight of a plasticiser the percentages being based on the weight of the powder, and spray drying the resulting dispersion to produce said powder.

2. A process as claimed in claim 1, wherein the amount of ethyl cellulose used is about 28% to 40% by weight.

3. A process as claimed in claim 1 or claim 2 wherein the plasticiser is dibutyl sebacate.

4. A process as claimed in claim 1 or claim 2 wherein the plasticiser is triethyl citrate.

5. A process for preparing a pharmaceutical dosage form for oral administration as a solid, which dosage form can be disintegrated by water within 10 seconds, which comprises incorporating a therapeutic taste neutral powder form of ibuprofen, prepared by a process as claimed in any one of claims 1 to 4, into a dosage form for oral administration as a solid, which dosage form can be disintegrated by water within 10 seconds, in a manner known per se.

6. A process for preparing a pharmaceutical dosage form for oral administration as a solid chewable taste neutral tablet containing ibuprofen which process comprises preparing a therapeutic taste neutral powder form of ibuprofen by a process as claimed in any one of claims 1 to 4 and then incorporating the powder into a solid chewable taste neutral tablet in a manner known per se.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 31 1570

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	CHEMICAL ABSTRACTS, vol. 95, no. 9, November 1981, page 382, abstract no. 156580m, Columbus, Ohio, US; & JP-A-81 46 837 (KOWA PHARMACEUTICAL INDUSTRY CO., LTD) 28-04-1981 * Abstract * ---	1-4	A 61 K 31/19 A 61 K 9/20 A 61 K 9/50
Y	CHEMICAL ABSTRACTS, vol. 102, no. 24, June 1985, page 349, abstract no. 209280k, Columbus, Ohio, US; A. KANNIKOSKI et al.: "Release of verapamil hydrochloride from granules coated with ethyl cellulose films. Part I", & ACTA PHARM. FENN. 1984, 93(3), 147-57 * Abstract * ---	1-4	
D,A	US-A-4 371 516 (G.K.E. GREGORY et al.) * Abstract * ---	5	
A	US-A-3 922 379 (B. FARHADIEH) * Abstract * -----	6	TECHNICAL FIELDS SEARCHED (Int. Cl.4) A 61 K 9/00 A 61 K 31/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-04-1989	DULLAART A.W.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(54) **Spray drying method and apparatus for concurrent particle coating.**

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NL-A- 8 602 952
US-A- 2 953 457
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EP 0 344 375 B1

Description

Background of the Invention.

This invention pertains to spray drying apparatus, especially to improvements in such apparatus which make it possible to coat the particulate matter, which is separated from a mixture of the material and liquid, with another substance such as lecithin.

Spray drying apparatus has been widely used in the food preparation industry for separating a liquid from solids or drying such products as milk, cream, instant coffee, vegetable juices and many other products. Typical drying apparatus comprises a chamber into which the liquid/solid mixture is sprayed concurrently with a stream of hot gas, usually hot filtered air. The exchange of heat with the fine droplets of the mixture causes the volatile fluid in the droplets to vaporize. The resulting dried solids settle on a porous conveyor belt in the bottom of the chamber. The solids are usually transported on the conveyor belt through a cooling chamber after which the agglomeration of solid particles or mat as it is called may be milled or otherwise processed. The drying entraining gas is drawn through the mat and porous belt, filtered and discharged to the atmosphere. Processes of this type are disclosed in US-A-4 116 756 and in Food Technology, vol. 27, No. 12, Dec. 1973, pages 18-26.

Some food or beverage particles after having been dried as described above are coated with substances to impart certain properties to them. Lecithin is one of the non-volatile coating substances which is material to the invention. Lecithination or coating of spray dried high-fat particles on the exterior of the particles is done in an attempt to make the particle hydrophilic rather than hydrophobic. If hydrophobic particles are coated with lecithin they are made wettable and therefore acquire the ability to sink and take on water and rehydrate quickly. This is an important property for such beverage and food products such as instant coffee, powdered milk and many other products that the consumer dissolves in water before using them.

Lecithin is a waxy hydroscopic phosphatide derived primarily from plant or vegetable sources. Soybean seed is a major source although there are other sources which yield different grades. Lecithin is also not easily oxidized so it is sometimes added to the exterior of powdered fat products to protect a readily oxidized fat from degrading by reacting with the oxygen in air.

Prior practice has been to apply the lecithin in a separate piece of equipment after the powdered product is removed from the dryer. Best results were obtained if the powdered product were held for a minimum of 24 hours but an even longer period such as 48 to 72 hours was desirable before lecithination was begun. The dried product was put into some bulk storage equipment and ultimately rewarmed in some auxilliary equipment before the lecithin was sprayed onto the exterior of the powder in a blender and/or in a fluid bed system where the powder particles would rotate from under the surface to the surface while a fine spray of lecithin mist would be applied to the powder particles.

One of the problems inherent in the conventional lecithination process is that the specialized equipment for performing the lecithination consumed a significant amount of plant space as well as the bulk storage, tote bins, rebagging or methods of holding the powder between the time it was produced and the time after which it could be lecithinated. Handling the powder to put it in storage and take it out and lecithinate it increased the probability of the product becoming contaminated. The additional equipment required for lecithinating represented a significant capital investment. The prior practice was also energy wasteful since the powdered product to be reheated to be lecithinated and then cooled so it could be packaged. Moreover, multiple handling of the dusty powder always resulted in some loss of product in the filters and air and powder separators of the other lecithination equipment.

In connection with conventional spray drying in which no conveyor belt is arranged in the bottom of the drying chamber it has been suggested to perform a lecithination in the drying chamber as an integrated part of the drying process.

Thus US-A-3126 289 describes a process in which lecithin is brought into contact with milk concentrate at the time of or immediately prior to atomization by means of a rotating atomizer wheel. However, this method does not ensure that all lecithin used will be present as a surface coating of the product, and any lecithin incorporated in the interior of the powder particles will have no "instantizing" effect on the powder. Besides, since the method envolves the use of a rotating atomizer wheel, it cannot be applied in connection with a drying system as the one dealt with in present specification which is based on nozzle atomization directed against the conveyor.

FR-A-2 398 525 discloses a process in which an ageous solution of lecithin is atomized countercurrently against the cloud of feed droplets ejected from an atomizer wheel. The turbulent conditions under which the spray of lecithin solution droplets meets the opposite directed droplets of feed ensure that a high percentage of the lecithin droplets collides with the feed droplets and thereby weting of the chamber walls with lecithin is avoided. How-

ever, the coating of the product particles will be less uniform than desired, and also this method can hardly be adapted to the drying system dealt with in the present specification.

Summary of the Invention

The present invention deals with a method of applying coating of a non-volatile substance to particles derived from a mixture of solid particles and liquid comprising the steps of:

spraying said mixture through at least one first stationary nozzle into a chamber along with a stream of heated gas to produce a mist of mixture droplets suspended in the gas to cause evaporation of the liquid from the solid particles in the droplets,

spraying said substance through at least one second stationary nozzle into said chamber concurrently with said gas and said mixture to form a mist of substance droplets having a substantially laminar flow in said gas stream so that the substance droplets contact said droplets of the mixture and resulting solid particles and deposit a coating of the substance on the particles, and directing the stream of gas toward a conveyor means to settle the thus coated particles on said conveyor means.

This method enables particle coating as an integrated part of the drying process also in connection with the use of a conveyor belt in the drying chamber, the concurrent, laminar flow conditions provide for a very uniform coating of all particles. Because said flow conditions are used in connection with a conveyor means covered with a powder layer on which any non-collided droplets of coating material will be absorbed, use of said favorable conditions can be made without formation of sticky deposits in the drying chamber.

The new method and apparatus will be illustrated herein as applied to coating solid particles with lecithin concurrently with separating the particles from a mixture of solid particles and liquid such as milk. It should be understood, however, that the method and apparatus are applicable to coating powder particles with other non-volatile liquids or oils, not only to provide a more wettable product, but in some cases to apply an encapsulating agent onto the surface tc reduce product oxidation and/or loss of particle flavor during storage.

A more detailed description of a preferred embodiment of the new particle coating apparatus and method will now be set forth in greater detail in reference to the drawings.

Description of the Drawings

FIGURE 1 is a schematic partial side elevation view of a spray drying apparatus in which the new particle coating device is incorporated and in which the new method of coating with lecithin can be performed;

FIGURE 2 is a diagram of the overall system for applying a lecithin coating to solid particulate material concurrently with drying the material;

FIGURE 3 is a diagram showing concentric conduits the central one of which conducts hot water and the outer one of which conducts a coating fluid such as lecithin in an oily vehicle;

FIGURE 4 is a plan view of the spray drying section of the apparatus in FIGURE 1; and

FIGURE 5 is a nozzle assembly that has an input for the coating material, such as lecithin and an input for pressured air for effecting atomization of the lecithin.

Description of a Preferred Embodiment

The part of the apparatus depicted in FIGURE 1 that is involved in simply spray drying a food substance such as powdered milk is known in the art and is described in U.S. Patent No. 4,116,756 which is assigned to the assignee of this application. The disclosure of this patent is incorporated herein by reference. This should not be interpreted to mean that the new spray coating apparatus is only usable with this particular spray drying apparatus for it can be used with spray drying apparatus which differs from that depicted in the patent.

For the sake of illustration, assume that a material such as milk is being spray dried and, in accordance with the invention, lecithin is being applied to the finally divided solids that result from separating the water from the milk.

The apparatus in FIGURE 1 is comprised of an enclosed primary stage spray chamber 10 above which there is a plenum 11 having a plurality of hot air inlet ports 12. Extending vertically downward through each port 12 is a spray nozzle 14 which is supplied from a header 15 with milk which is a mixture of liquid and solid materials that are to be separated with the spray drying apparatus. The liquid and solid mixture is pumped to the header 15 through a pipe 16. The pump and the storage reservoir for the milk are not shown.

The air that is forced through inlet ports 12 is derived from the atmosphere through a filter unit 17, a blower 18, a heater unit 19 which couples to plenum chamber 11 by means of a duct 20.

Thus, when the basic drying process is being carried out, the mixture, such as milk, to be dried contains solid material either, or both, dissolved or suspended in it and this material is atomized by nozzles 14 and entrained in the hot air streams flowing through inlet ports 12. The liquid that is still in proximity with the nozzles is in the form of wet

droplets. These droplets are entrained in the heated air passing downwardly through ports 12 from plenum 11. As the solid particles pass downwardly the liquid is evaporated from them. They are finally forced by the air stream to settle on a porous belt 25 which is described in detail in the cited patent. The belt runs on rollers 26, 27, 28, 29 and 30. Roller 30 may be driven rotationally through a speed reducer and an electric motor, neither of which are shown. Driven roller 30 causes belt 25 to translate. The solid material mat 31 in an adequately dried state builds up on conveyor belt 25 and is finally transported to a chamber 32. The particles deposited on belt 25 are weakly bonded to each other and form an aggolomerated mass commonly referred to as a mat or powder cake. Once the mat begins to form on the belt the heated drying air will begin to stream over and around the particles and through the tiny interstices between the particles in the mat and then through the pores in the belt. The drying air then flows into chambers beneath the belt and then out to the atmosphere through ducts 36, 37 and 38 and exhaust blowers 39, 40 and 41.

The mat that is formed in the primary drying chamber 10 is transported on porous conveyor belt 25 to a retention chamber 42 in which heated air from both the adjacent main sprayer 10 and a second stage drying chamber 43 is drawn through the mat 31 and porous belt 25 into a chamber 44 below belt 25 and then out to the atmosphere through a duct 45 and an exhaust blower 80.

Mat 31 then passes from chamber 42 to the second stage drying chamber 43. Heated air is supplied to the top of chamber 43 through filter unit 17, a blower 47, a heater 48 and a duct 49. Heated air is drawn through the mat and belt from chamber 43 into a chamber 50 below the belt and then out to an atmosphere through a duct 51 and a blower 52.

The mat 31 then passes from chamber 43 to a final cooling chamber 53. Air from the atmosphere is drawn through filter unit 17, a cooling and dehumidifying unit 54 and a conduit 55.

From the cooling stage chamber 53 the mat 31 passes to the end of the belt through chamber 32 where it is cut and crushed into small particles by a suitable device identified by the numeral 60. The product is then sized and transmitted from the apparatus by suitable mechanism shown schematically and identified by reference numeral 61. Any fine particles which pass through the belt through the processing as described above are collected by suitable cyclone collection units 62-66, which particles are then recirculated back to chamber 42 through a conduit 67 for reprocessing.

In accordance with prior art practices of coating powder particles with a non-volatile substance such as lecithin, the dried and ground solids accumulated in the final collection chamber 60 at the end of the conveyor belt would be held for conditioning preparatory to coating the particles with lecithin. As mentioned in the introductory paragraphs of this specification, prior art methods for lecithination produced more uniformly and tenaciously coated particles if the particles were simply held in storage for at least forty-eight hours. Then if the materials were bagged for storage or held in bins, they were conducted to the lecithination apparatus which might have been a fluidized bed. Regardless of the type of apparatus used, the material had to be rebagged or placed in some other types of containers for storage or shipping as the case may be. In accordance with the invention, lecithination is accomplished concurrently with the spray drying procedure. The new direct lecithination method will now be described in greater detail.

Attention is invited to FIGURE 1 again and, particularly, to the vicinity of the plenum 11. Beneath the plenum and arranged periodically between the nozzles 14 through which the fluid and solid mixture is sprayed are another set of nozzles 70 which spray the non-volatile lecithin material into drying chamber 10. In actuality, pure lecithin is not sprayed but a mixture of lecithin and some low melting point vegetable and/or animal fat oil is sprayed. These oils are pre-blended with the lecithin so that the viscosity and surface tension of the lecithin is reduced, otherwise it is nearly impossible to atomize the lecithin fine enough to get good distribution in the drying chamber 10. In prior art lecithination, the lecithin is also usually mixed in some other oil to reduce its surface tension to thereby enhance its flowability and attraction to the surface of the dry particulates. In accordance with the invention, the lecithin, as it and its oily vehicle will be called, is projected through nozzles 70 which create a fine mist of lecithin in the drying chamber 10. The direction in which the lecithin is projected is indicated by the diverging lines 71 but, in actual practice, the lecithin disperses and creates a fine nebulous mist in the chamber. The pressure applied to the lecithin is held low enough so that its velocity when emitted from the nozzles is quite low. Hence, flow is laminar rather than turbulent which is desirable. The pressurized lecithin is conducted to nozzles 70 by pipes marked 72 in FIGURE 1. There are also some pipes 73 which deliver pressurized air to the nozzles for bringing about atomization of the lecithin. Experience has shown that these two-fluid nozzles 70 are preferred but a single fluid or high pressure nozzle could also be used. The use of pressured air overcomes a problem of nozzle plugging that might occur because of small amounts of thick material in the lecithin itself. The pressurized air

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assists in atomizing the lecithin and in keeping the nozzle orifices clear.

A more complete diagram of the system for applying a coating of a non-volatile substance to powder appears in FIGURE 2. The nozzles for spraying the non-volatile lecithin and its liquid vehicle into the drying chamber 10 are marked 70 as they are in FIGURE 1. The lecithin feed pipes to the nozzles 70 are again marked 72 and the pressured air feed pipes are marked 73. The details of the atomizing nozzles 70 are shown in FIGURE 5. The air pipes 73 leading to the nozzles in FIGURE 2 connect to a header 74 which are connected to the outlet of a filter 75 that is supplied with compressed air from a source, not shown, through inlet pipe 76.

In FIGURE 2 a quantity of lecithin 77 is contained in a tank 78. The lecithin is supplied to tank 78 through an inlet pipe 79 which is fed from a bulk storage container, not shown. There is a jacket 80 surrounding tank 78 in spaced relationship to provide a chamber 81 through which hot water flows to raise the temperature of the lecithin to a level that brings about a satisfactorily low viscosity and surface tension so that the lecithin will spread or flow on the particles that are being coated. By way of example and not limitation, the lecithin may be warmed to about 65 °C (about 150 degrees F).

The source of hot water is symbolized by a boiler marked 82 associated with a heat source 83. There is an inlet pipe 84 for supplying water to the boiler. A circulating pump 85 has its inlet pipe 86 connected to the boiler. The outlet pipe 87 runs concentrically with a larger lecithin conducting output pipe 88. The end 89 of hot water pipe 87 discharges the hot water into the jacket 81 and it circulates about the jacket to heat the lecithin 77 in tank 78. The heated water is then discharged from jacket 81 into the end 90 of a water pipe section 91 that runs concentrically inside of surplus lecithin return pipe 92. The hot water then flows to and through a lecithin heating coil 93 which is installed in a tank 94. After passing through heating coil 93, the warmed water flows concentrically with the lecithin feed pipe 95 leading to tank 94. The water, after having given up some of its heat is returned to boiler 82 by way of pipe 96. Thus, a closed warm water circulatory system has been defined.

The lecithin circuit is concurrent with the hot water pipe. The outlet pipe 88 from the bottom of tank 78 is the inlet to a lecithin pump 97. The outlet pipe from pump 97 is marked 98 and this pipe conducts lecithin through a check valve 99 for discharge into tank 94. The lecithin that is not delivered to the nozzles 70 is recirculated from tank 94 by means of a pipe 100 that returns the lecithin 77 to holding and warming tank 78.

The lecithin flows through the bottom outlet 101 of tank 94 to several header pipes, two of which, 102 and 103 are depicted in FIGURE 2. The lecithin is supplied through pipes 72 to nozzles 70 from the outlets of a plurality of pumps which are collectively designated by the reference numeral 104. In this particular model, there are nine pumps. These are reciprocating pumps and they are all driven by a single electric motor 105. The motor is supplied with alternating current from a commercially available frequency converter 106. The speed of the motor and, hence, the output from the individual pumps 104 is governed in part by the frequency of the alternating current supplied to motor 105. As is well known, as frequency is increased, motor speed increases and, conversely, when frequency is decreased, the motor speed decreases. As stated, pumps 104 are reciprocating pumps and further individual control over the pressure applied to the lecithin emitting nozzles can be obtained by adjusting the stroke length of the pumps by means which are not shown in detail but which are readily evident on variable output pumps which are commercially available. There are valves 107 on the inlet lines to the pumps. Thus, there are two ways of controlling the amount of lecithin delivered from the pump outputs, namely, changing the motor frequency to change the output of all pumps by a fixed amount and changing the stroke of the individual pumps to get the best mist distribution in the drying chamber 10 that can obtained for the particular geometry of the chamber and nozzle arrangement.

The way the nozzles for the product being dried and for the emission of lecithin are deployed is illustrated in FIGURE 4.

The system could be provided with one motor driven feed pump to supply several lecithin nozzles. However, in such case it is more difficult to control the quantity of the lecithin mist relative to the zone within the drying chamber that the particular nozzle supplies. The objective in any case is to develop a quantity of lecithin mist that is uniformly proportional to the density of the droplets of the mixture that are giving up their fluid by evaporation.

Nozzles 14 spraying in the liquid-solids mixtures and the nozzle 70 spraying in the lecithin mist, the lecithin droplets and the mixture droplets collide to bring about coating with lecithin. The coated particles drop down to the porous conveyor belt 25 to form the mat 31 which as has previously described is conveyed to the output chamber 32 where it can be milled, sized and bagged or conveyed to storage bins in preparation for bagging. The solid food particles, now coated with lecithin are much more hydrophilic than they would be if they were not coated with lecithin. A thorough and

uniform particle coating results from the concurrent spray method. As a result, when a food product such as beverage whitener or instant dry milk is so treated, it wets rapidly and sinks and dissolves or is otherwise distributed in the water used for reconstituting to the original product before it was dried.

The apparatus and method have been illustrated in reference to coating milk solids with lecithin. Those skilled in the art will appreciate, however, that the apparatus and method have a variety of applications, especially in the food processing industries. For example, sesame seed oil is usable in the apparatus as a spray coating substance for food particles. This oil has non-volatile and non-oxidative properties which can preserve the desirable properties of the treated product. Propylene glycol is another edible oil that can be used as the coating substance for a variety of products.

Claims

1. A method of applying coating of a non-volatile substance to particles derived from a mixture of solid particles and liquid comprising the steps of:

   spraying said mixture through at least one first stationary nozzle into a chamber along with a stream of heated gas to produce a mist of mixture droplets suspended in the gas to cause evaporation of the liquid from the solid particles in the droplets,

   spraying said substance through at least one second stationary nozzle into said chamber concurrently with said gas and said mixture to form a mist of substance droplets having a substantially laminar flow in said gas stream so that the substance droplets contact said droplets of the mixture and resulting solid particles and deposit coating of the substance on the particles, and directing the stream of gas toward a conveyor means to settle the thus coated particles on said conveyor means.

2. The method according to claim 1 wherein the substance is converted to droplets by emitting said substance from a nozzle along with pressurized air.

3. The method according to claim 1 wherein the conveyor means is a porous belt so said particles after having been coated with said substance settle on said belt and said gas passes through said porous belt.

4. Apparatus for coating with a non-volatile substance solid particles derived from a mixture of solid particles and liquid, comprising:

   a drying chamber,

   a means for directing a stream of heated gas into said chamber,

   at least one first stationary nozzle for spraying said mixture into said chamber and forming a mist of mixture droplets entrained in said gas so said heated gas evaporates said liquid from said solid particles,

   at least one second stationary nozzle arranged for spraying said substance into said chamber concurrently with said gas and said mixture and forming a mist of the substance having a substantially laminar flow entrained in said gas for contacting said mixture droplets and solid particles to coat said particles with the substance, and

   conveyor means toward which said gas stream is directed so the coated particles settle on said conveyor means.

5. The apparatus according to claim 4 wherein said conveyor means comprises a porous belt on which said particles settle and through which said gas flows.

6. The apparatus according to claim 4 including:

   a plurality of pumps having inlets respectively coupled to a source of said substance and outlets coupled to said at least one nozzle respectively, for said pumps to pressurize said substance sprayed from said second nozzle means.

7. The apparatus according to claim 4 wherein the individual second nozzles have a jet from which said substance is emitted and a jet from which pressurized air is emitted into the substance to enhance atomization of said substance,

   means coupling the substance emitting jet to a source of substance and means coupling said air emitting jet to a source of pressurized air.

8. The apparatus according to claim 4 including:

   a plurality of adjustable capacity pumps having inlets respectively coupled to a source of the substance and outlets coupled to the second nozzle means, respectively,

   a single electric motor and means coupling said motor to said plurality of pumps for driving said pumps simultaneously.

9. The apparatus according to claim 8 wherein said electric motor is an alternating current motor, and including

   an adjustable frequency power supply coupled to said motor for energizing the motor

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and causing said motor to run at a speed proportionalt to the frequency of said supply so that by adjusting said frequency the output of all of said pumps can be changed simultaneously.

10. The apparatus according to claim 4 wherein said second nozzle means are arranged intermittently with said first nozzle means at the top of said chamber and the spray from said first and second nozzle means and said heated gas are directed toward said conveyor means which is at the bottom of the chamber.

11. The apparatus according to any one of claims 6, 7 or 9 including:

a container having an outlet communicating with the inlets of said pumps,

a tank having an inlet for being supplied with said substance,

a pipe circuit connecting said tank to said container and said container to said tank and pump means in said circuit for circulering the substance between the tank and container,

a jacket on said tank,

a hot water reservoir and a pump having an inlet coupled to said reservoir and an outlet coupled to said jacket for heating the substance in the tank, and

heating coil means in said container for the substance and a pipe circuit connecting said jacket to said coil means and said coil means to said reservoir.

12. The apparatus according to claim 4 including a pump having an inlet for said coating substance and an outlet connected to said second nozzle means.

13. The method according to any of one of claims 1, 2 or 3 wherein said substance is a blend of lecithin and a low melting point edible oil.

Patentansprüche

1. Verfahren zum Auftragen einer Beschichtung einer nicht flüchtigen Substanz auf aus einem Gemisch von festen Teilchen und Flüssigkeit stammenden Teilchen, umfassend die Stufen von:

Zerstäuben des Gemisches durch mindestens eine erste stationäre Düse in eine Kammer zusammen mit einem Strom erhitzten Gases zur Erzeugung eines Nebels im Gas suspendierter Tropfen des Gemisches zwecks Verdampfung der Flüssigkeit von den festen Teilchen der Tropfen,

Zerstäuben der Substanz durch mindestens eine zweite stationäre Düse in erwähnte Kammer im Gleichstrom mit dem Gas und dem Gemisch zur Bildung eines Nebels von Substanztropfen mit im wesentlichen laminaren Fliessen im Gasstrom, wobei die Substanztropfen mit den Gemischtropfen in Kontakt kommen und zu festen Teilchen führen und eine Schicht der Substanz auf den Teilchen ablagern, und Leiten des Gasstroms zu einem Fördermittel zwecks Absetzen der somit beschichteten Teilchen auf dem Fördermittel.

2. Verfahren nach Anspruch 1, worin die Substanz durch Abgabe aus einer Düse zusammen mit Druckluft in Tropfen umgewandelt wird.

3. Verfahren nach Anspruch 1, worin das Fördermittel ein poröses Band ist, sodass sich die Teilchen nach erfolgtem Beschichten mit der Substanz auf dem Band absetzen, und das Gas durch das poröse Band passiert.

4. Vorrichtung zum Beschichten von aus einem Gemisch von festen Teilchen und Flüssigkeit stammenden festen Teilchen mit einer nicht flüchtigen Substanz, umfassend:

eine Trockenkammer,

ein Mittel zum Leiten eines Stroms erhitzten Gases in die Kammer,

mindestens eine erste stationäre Düse zum Zerstäuben des Gemisches in die Kammer und Bildung eines im Gas mitgeführten Nebels von Gemischtropfen, sodass das erhitzte Gas die Flüssigkeit von den festen Teilchen verdampfen lässt,

mindestens eine zweite stationäre Düse zum Zerstäuben der Substanz in die Kammer im Gleichstrom mit dem Gas und dem Gemisch und zur Bildung eines in dem Gas mitgeführten Nebels der Substanz mit einem im wesentlichen laminaren Fliessen zwecks Kontakt der Gemischtropfen und festen Teilchen zum Beschichten der Teilchen mit der Substanz, und

ein Fördermittel, gegen welches der Gasstrom geleitet wird, damit sich die beschichteten Teilchen an dem Fördermittel absetzen.

5. Vorrichtung nach Anspruch 4, demzufolge das Fördermittel ein poröses Band umfasst, auf welchem sich die Teilchen absetzen und durch welches das Gas fliesst.

6. Vorrichtung nach Anspruch 4, umfassend:

eine Mehrzahl von Pumpen mit Einläufen, von denen jeder an eine Quelle der Substanz angeschlossen ist bzw. Ausläufen, die an er-

wähnte zumindest eine Düse gekoppelt sind, wobei die Pumpen die von der zweiten Düse zu zerstäubende Substanz zusammenpressen.

7. Vorrichtung nach Anspruch 4, worin in den einzelnen zweiten Düsen die Substanz durch einen Strahl abgegeben wird und zwecks Verbesserung der Zerstäubung der Substanz ein Strahl Druckluft in die Substanz abgegeben wird,

Mittel zum Anschliessen des substanz-abgebenden Strahls an eine Substanzquelle und Mittel zum Anschluss des luftabgebenden Strahls an eine Quelle von Druckluft.

8. Vorrichtung nach Anspruch 4, umfassend:

eine Mehrzahl einstellbarer Leistungspumpen mit an eine Substanzquelle angeschlossenen Einläufen bzw. an die zweite Düse angeschlossenen Ausläufen,

einen einfachen Elektromotor und Mittel zum Anschluss des Motors an die Mehrzahl der Pumpen zum gleichzeitigen Pumpenantrieb.

9. Vorrichtung nach Anspruch 8, worin der Elektromotor ein Wechselstrommotor ist, umfassend:

eine an den Motor angeschlossene Stromversorgung mit einstellbarer Frequenz zum Antrieb und Laufen des Motors bei einer zur Versorgungsfrequenz proportionalen Geschwindigkeit, sodass beim Einstellen der Frequenz die Ausgangsleistung aller Pumpen gleichzeitig geändert werden kann.

10. Vorrichtung nach Anspruch 4, worin die zweite Düse mit der ersten Düse oben in der Kammer intermittierend angeordnet ist, und die Zerstäubung von der ersten und der zweiten Düse sowie das erhitzte Gas zu dem am Boden der Kammer befindlichen Fördermittel geleitet werden.

11. Vorrichtung nach einem der Ansprüche 6, 7 oder 9, umfassend:

einen Behälter mit einem Auslauf, der mit den Einläufen der Pumpen zusammenarbeitet,

einen Tank mit einem Einlauf zur Versorgung mit erwähnter Substanz,

ein Rohrsystem, das den Tank mit dem Behälter und den Behälter mit dem Tank verbindet, sowie im Rohrsystem angeordnete Pumpen zum Zirkulieren der Substanz zwischen dem Tank und dem Behälter,

einen Mantel auf dem Tank,

ein Warmwasser-Reservoir und eine Pumpe mit einem an das Reservoir angschlossenen Einlauf und einen an den Mantel angeschlossenen Auslauf zum Erhitzen der im Tank befindlichen Substanz, und

eine im Behälter für die Substanz angeordnete Heizspirale und ein Rohrsystem, das den Mantel mit der Heizspirale und die Heizspirale mit dem Reservoir verbindet.

12. Vorrichtung nach Anspruch 4, umfassend eine Pumpe mit einem Einlauf für die Beschichtungssubstanz sowie einen an die zweite Düse angeschlossenen Auslauf.

13. Verfahren nach einem der Ansprüche 1, 2 oder 3, wonach die Substanz ein Gemisch aus Lecithin und einem Speiseöl mit niedrigem Schmelzpunkt ist.

Revendications

1. Procédé d'application d'un enrobage d'une substance non volatile sur des particules provenant d'un mélange de particules solides et d'un liquide, comportant les étapes suivantes:

pulvérisation dudit mélange par au moins une première buse stationnaire dans une chambre avec un courant de gaz chaud pour produire un brouillard de gouttelettes de mélange suspendues dans le gaz pour provoquer l'évaporation du liquide des particules solides dans les gouttelettes,

pulvérisation de ladite substance par au moins une seconde buse stationnaire dans ladite chambre simultanément avec ledit gaz et ledit mélange pour former un brouillard de gouttelettes de substance en un écoulement essentiellement laminaire dans ledit courant de gaz si bien que les gouttelettes de substance viennent en contact avec les gouttelettes de mélange et les particules solides résultantes et déposent un enrobage de substance sur les particules, le courant de gaz étant dirigé vers un convoyeur pour y déposer les particules ainsi enrobées.

2. Procédé selon la revendication 1, selon lequel la substance est transformée en gouttelettes par émission de ladite substance par une buse avec de l'air comprimé.

3. Procédé selon la revendication 1, selon lequel le convoyeur est un tapis poreux si bien qu'après avoir été enrobées avec ladite substance, les particules se déposent sur ledit tapis, le gaz passant à travers le tapis poreux.

4. Appareil pour enrobage de particules solides provenant d'un mélange de particules solides

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et de liquide avec une substance non volatile, comprenant:

une chambre de séchage,

un moyen pour diriger un courant de gaz chaud dans ladite chambre,

au moins une première buse stationnaire de pulvérisation dudit mélange dans la chambre et de formation d'un brouillard de gouttelettes de mélange entraînées par le gaz si bien que ce gaz chaud provoque l'évaporation du liquide des particules solides,

au moins une seconde buse stationnaire disposée pour pulvériser la substance dans la chambre simultanément au gaz et au mélange et pour former un brouillard de substance en un écoulement essentiellement laminaire entraîné dans ledit gaz pour venir en contact avec les gouttelettes de mélange et les particules solides afin d'enrober ces particules avec la substance, et

un moyen convoyeur vers lequel le courant de gaz est dirigé pour y déposer les particules enrobées.

5. Appareil selon la revendication 4, dans lequel ledit moyen convoyeur comprend un tapis poreux sur lequel les particules se déposent et à travers lequel le gaz s'écoule.

6. Appareil selon la revendication 4, comportant:

un nombre de pompes dont les entrées respectives sont branchées sur une source de ladite substance et dont les sorties sont branchées sur au moins une buse respective, pour que les pompes pressurisent ladite substance pulvérisée par ladite seconde buse.

7. Appareil selon la revendication 4, selon lequel les secondes buses individuelles ont un jet à partir duquel ladite substance est émise et un jet à partir duquel l'air comprimé est émis dans la substance afin de renforcer l'atomisation de cette substance,

des moyens accouplant le jet émetteur de substance à une source de substance et des moyens accouplant le jet émetteur d'air à une source d'air comprimé.

8. Appareil selon la revendication 4, comportant:

un nombre de pompes à capacité réglable, dont les entrées respectives sont branchées sur une source de ladite substance et dont les sorties respectives sont branchées sur lesdites secondes buses,

un moteur électrique unique et des moyens d'accouplement dudit moteur auxdites pompes afin de les mettre en fonctionnement simultané.

9. Appareil selon la revendication 8, dans lequel le moteur électrique est un moteur à courant alternatif, et comprenant:

une alimentation à fréquence variable accouplée au moteur pour l'actionner et l'amener à fonctionner à une vitesse proportionnelle à la fréquence de l'alimentation si bien que par réglage de la fréquence, le débit de l'ensemble des pompes peut être modifié simultanément.

10. Appareil selon la revendication 4, dans lequel les secondes buses sont disposées en alternance avec les premières buses dans le haut de la chambre et la pulvérisation provenant desdites premières et secondes buses ainsi que le gaz chauffé sont dirigés vers le moyen convoyeur disposé dans le fond de la chambre.

11. Appareil selon l'une quelconque des revendications 6, 7 ou 9, comprenant:

un récipient doté d'une sortie communiquant avec les entrées desdites pompes,

un réservoir doté d'une entrée pour son alimentation avec ladite substance,

un circuit de tubes reliant ledit réservoir audit récipient et ledit récipient audit réservoir et des moyens de pompage dans ledit circuit pour faire circuler la substance entre le réservoir et le récipient,

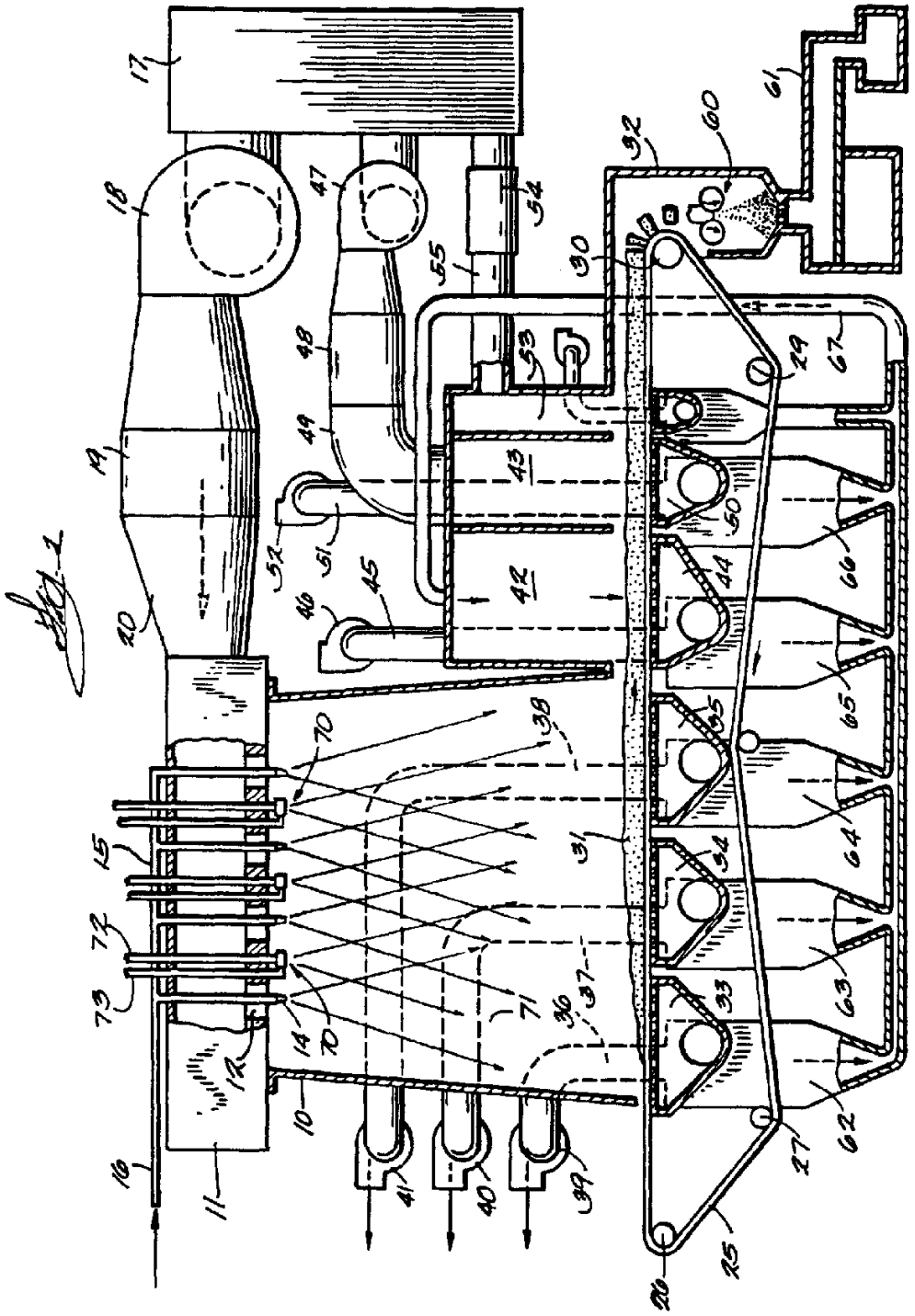
une enveloppe entourant ledit réservoir,

un réservoir d'eau chaude et une pompe dont l'entrée est reliée à ce réservoir et dont la sortie est reliée à ladite enveloppe pour chauffer la substance dans le réservoir, et

une spirale de chauffage située dans le récipient à substance, un circuit de tubes reliant l'enveloppe à ladite spirale et cette spirale audit réservoir.

12. Appareil selon la revendication 4, comprenant une pompe dotée d'une entrée pour ladite substance d'enrobage et d'une sortie reliée auxdites secondes buses.

13. Procédé selon l'une quelconque des revendications 1 à 3, selon lequel ladite substance est un mélange de lécithine et d'huile comestible à faible point de fusion.



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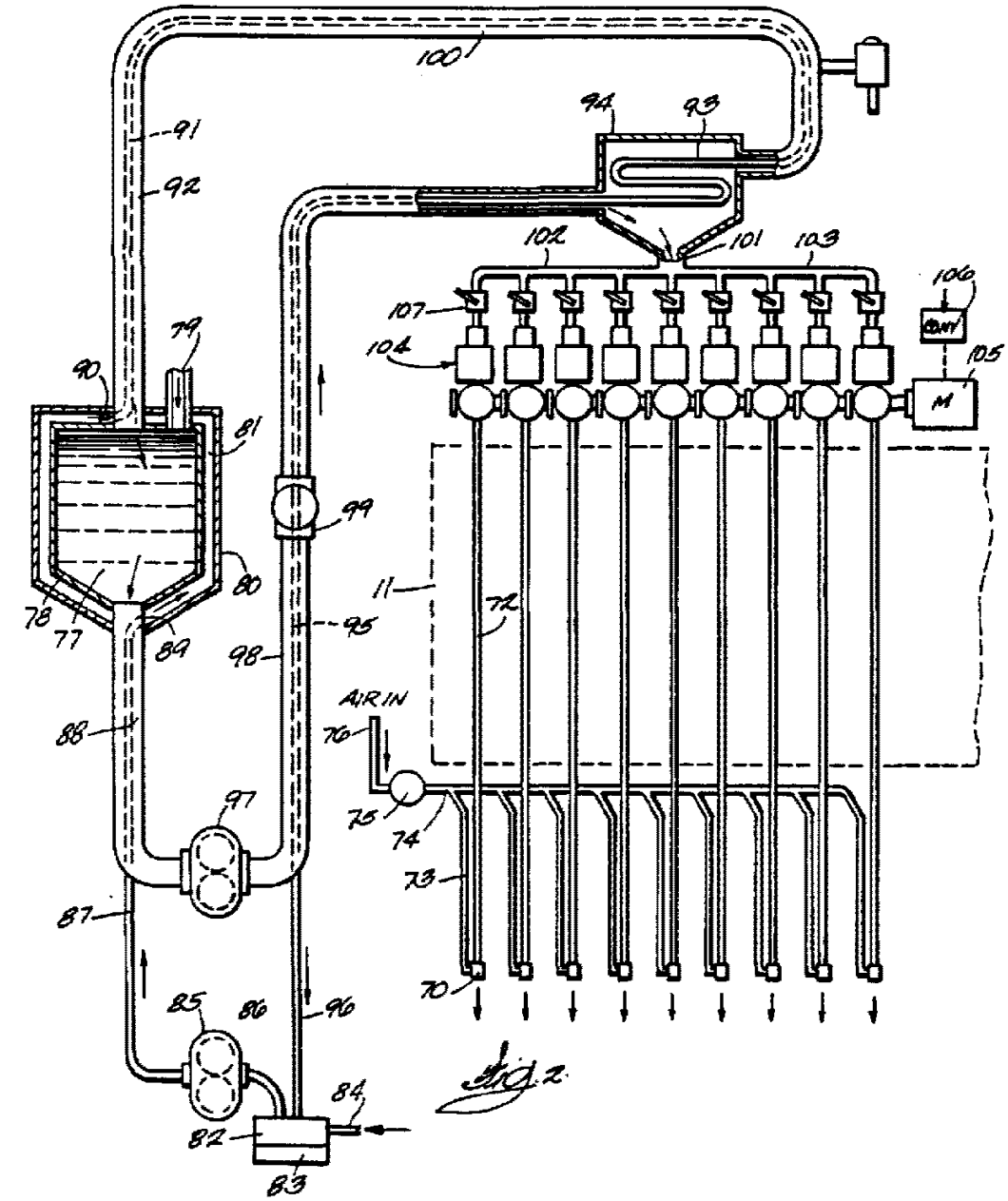


Fig. 2.

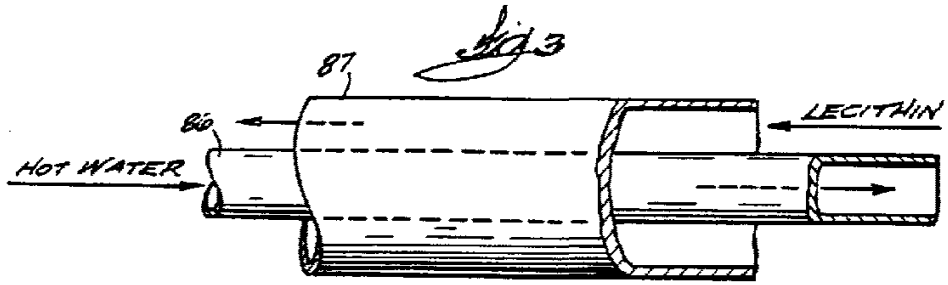


Fig. 3

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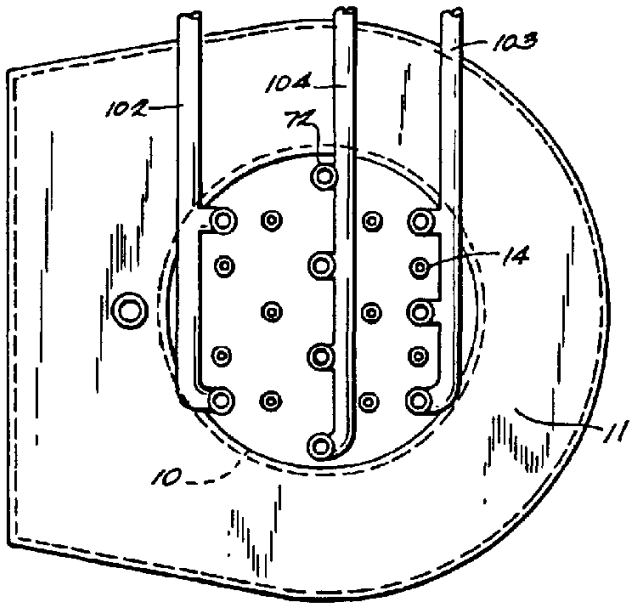


Fig. 4

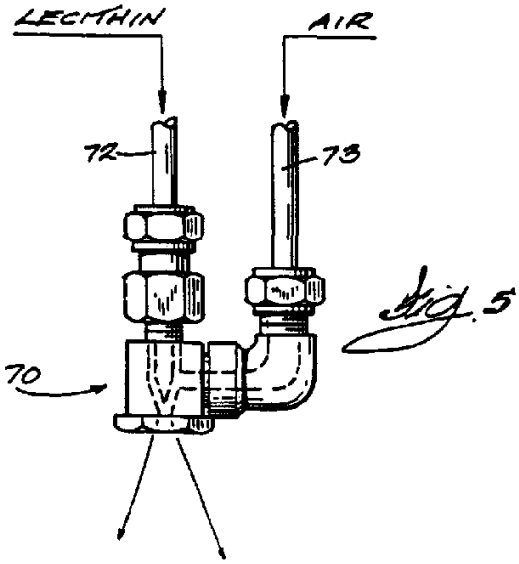


Fig. 5

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(54) **Continuous coupled jet-cooking/spray-drying process and novel pegelatinized high amylose starches prepared thereby**

Kontinuierliches gekoppeltes Dampfkochen/Sprühtrocknungsverfahren und die damit hergestellten pregelatinisierten, hohe Amylose enthaltenden Stärken

Procédé continu couplé de cuisson à vapeur/pulvérisation par séchage, et les amidons prégélatinisés riches en amylose ainsi obtenus

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Description

This invention relates to a process for jet-cooking and spray-drying water-dispersible or water-soluble polymers, especially high viscosity starches such as high amylose starches. It also relates to the unique pregelatinized high amylose starches produced thereby.

Pregelatinized starches (i.e., cold-water-dispersible starches) are typically prepared by thermal, chemical, or mechanical gelatinization. The term "gelatinized" or "cooked" starch refers to swollen starch granules which have lost their polarization crosses and which may or may not have lost their granular structure.

The thermal processes generally used to prepare such starches include batch cooking, autoclaving, and continuous cooking processes in a heat exchanger or jet-cooker. The thermal dispersion of a granular starch in water involves a complex mechanism. See the discussion at pp. 427-444 in Chapter 12, by Kruger & Murray of Rheology & Texture in Food Quality, Edited by T.M. DeMan, P.W. Voisey, V.F. Rasper, and D.W. Stanley (AVI Publishing, Westport, Conn. 1976), at pp. 449-520 in Chapter 21 of Starch: Chemistry & Technology, Vol. 2, edited by R.L. Whistler (Academic Press, New York, New York 1967) and at pp. 165-171 in Chapter 4 by E.M. Osman of Food Theory and Applications, edited by P.C. Paul and H.H. Palmer (John Wiley & Sons, Inc., New York, NY 1972). The process begins at the gelatinization temperature, as water is absorbed into the starch granules, and continues as the hydrated granules swell and disrupt into smaller granule fragments until the starch finally approaches a molecular dispersion. The viscosity of the cook changes significantly during this process, increasing as the granules hydrate and swell and decreasing as the granular fragments are reduced in size. An appropriate amount of shear aids in breaking down the swollen granular fragments to give a molecular dispersion without substantial molecular degradation.

Pregelatinized starches are typically prepared by spray-drying, drum-drying, or extrusion.

Drum-drying involves simultaneously cooking and drying a starch slurry or paste on heated, rotating drums. Cooking and drying are accomplished over a period of time as determined by the temperature and rotation rate of the drums. The dried sheets are scraped off the drum with a metal knife and then ground. This process can be conveniently carried out at high solids content (typically about 43% maximum). The disadvantage of drum-drying is that this method generally only partially disperses the starch (i.e., the starch is not completely gelatinized) and this can result in poorly dispersible powders having undesirable textures when redispersed.

Extrusion may also be used to simultaneously cook and dry starches (see US-A-3,137,592). This method involves the physical working of a starch-water mixture at elevated temperature and pressure, causing the gelatinization of the starch, followed by expansion during flashing off the water after exiting from the extruder. The temperature and pressure are generated by mechanical shear between the rotating screw (auger) and cylindrical housing (barrel) of the extruder. Cooking is accomplished with both thermal and mechanical energy as the starch is forced through the system. This typically results in high viscosity during processing due to incomplete cooking and the final products are typically degraded due to molecular breakdown caused by excessive shear. Upon redispersion, the powders can give undesirable grainy textures, especially when low moisture starches are processed, due to incomplete dispersion during cooking. When starch is processed in the presence of additional water, a further drying step is required after the extrudate exits the extruder. This extended drying time further exaggerates the undesirable textures upon redispersion.

The following patents describe various processes for preparing pregelatinized starches.

US-A-1,516,512 describes a process for modifying starch in which starch slurries are forced through a heated pipe coil and then through a spraying orifice into a drying chamber. The slurries are processed with or without acid. The slurries are forced through the coil at excessively high pressures (e.g., $6.9 \cdot 10^6$ Nm^{-2} (1000 lbs.)) in order to insure against the possibility of vaporizing the liquid under treatment. Steam is maintained at $2.4\text{-}7.5 \cdot 10^5$ Nm^{-2} (35-110 pounds) of pressure. The temperature of the air introduced into the drying chamber is about 121°C (250°F), which is reduced to about 96°C (204°F) at the point of evaporation. The resulting starches are hydrolyzed and are about 15-75% soluble in cold water.

US-A-1,901,109 describes a spray-drying process in which starch slurries are atomized into a stream of heated air containing water vapor in such amount that vaporization of the water from the atomized particles occurs at a temperature above the gelatinization temperature of the starch and below the temperature at which further alteration (e.g., hydrolysis) occurs. The process can be carried out with or without a chemical gelatinization agent.

US-A-3,630,775 describes a spray-drying process in which a starch slurry is maintained under pressure during heating and continued under pressure through the atomization step. The pressure is interdependent with viscosity, temperature, and apparatus. The pressure requirement is that necessary for atomization and is in excess of that necessary to prevent vaporization of water in a slurry of high solids at elevated temperatures. The heating time is that which is sufficient to allow substantially complete gelatinization and solubilization of the starch if previously ungelatinized. Typically, the slurries (10-40% solids) are preheated to 54-171°C (130°-340°F), pumped under $1.4\text{-}4.7 \cdot 10^7$ Nm^{-2} (2,000-6,800 psi) of pressure through a continuous tubular heat exchanger, and heated to 182°-304°C (360-580°F)(which result in starch temperatures of 163-232°C - 325-450°F). Retention time of the starch in the cooker is 1.0-2.5 minutes. A conventional spray-dryer with a pressure type atomizing nozzle is used. The resulting starches are characterized as having less than 12% moisture, greater than 528 kg/m³ (33 lb/ft³) bulk density, and greater than 50% cold-water solubility.

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US-A-4,280,851 describes a spray-drying process for preparing granular pregelatinized starches. In this process a mixture of the granular starch in an aqueous solvent is cooked or gelatinized in an atomized state. The starch which is to be cooked is injected through an atomization aperture in a nozzle assembly to form a relatively finely-divided spray. A heating medium is also injected through an aperture in the nozzle assembly into the spray of atomized material so as to heat the starch to the temperature necessary to gelatinize the starch. An enclosed chamber surrounds the atomization and heating medium injection apertures and defines a vent aperture positioned to enable the heated spray of starch to exit the chamber. The arrangement is such that the lapsed time between passage of the spray of starch through the chamber, i.e., from the atomization aperture and through the vent aperture, defines the gelatinization time of the starch. The resulting spray-dried, pregelatinized starch comprises uniformly gelatinized starch granules in the form of indented spheres, with a majority of the granules being whole and unbroken and swelling upon rehydration. Nozzles suitable for use in the preparation of these starches are also described in US-A-4,610,760.

US-A-3,086,890 describes a process for preparing a pregelatinized isolated amylose powder. It involves autoclaving a slurry of an isolated amylose having an intrinsic viscosity of 1.3-2.9 at 191°C (375°F) under $3.4 \cdot 10^4$-$9.7 \cdot 10^5$ Nm^{-2} (5-140 psig) of pressure for 1-60 minutes at 0.1-25% solids, cooling the dispersion to 90°C (194°F), and drum-drying on a 110-200°C (230-392°F) surface. The retention time on the drum is 40-75 seconds using a nip gap of 0.0025cm (0.001 inch) or less. The resulting powders have amorphous X-ray diffraction patterns, intrinsic viscosities of 1.3-2.9, and form irreversible gels when redispersed.

Pregelatinized starches may be made by a two step spray-drying process which is in current industrial use. Modifications of this conventional process are described in US-A-2,314,459 and US-A-3,332,785. In the typical process an aqueous starch slurry is cooked, usually by atmospheric vat cooking or by cooking in a heat exchanger or by steam injection jet-cooking, held at atmospheric pressure in a tank (often a cooking tank in batch processes or a receiver tank for pressurized cooking processes), and subsequently spray-dried. The post-cooking holding period allows the batchwise addition of additives, temperature regulation, and/or cooking at rates which do not match the spray-dryer capacity. On exiting the holding tanks the temperature of the feed to the spray-dryer may range from 38-93°C (100-200°F). Atomization is effected by a single fluid pressure nozzle, a centrifugal device, or a pneumatic nozzle. This process is usually limited to "thin-cooking starches", i.e., converted starches where the polymeric structure has been degraded by acid hydrolysis, enzymatic degradation, oxidation and/or high levels of mechanical shear. Converted starches can be used at higher solids because their pastes are lower in viscosity and can be atomized. The cooks of unmodified starches are difficult to atomize because of their high viscosity and therefore, if spray-dried, are processed at low solids. Another limiting factor of conventional processes is that, at temperatures achieved at atmospheric pressure, many polymers associate and/or retrograde causing an increase in viscosity. See US-A-3,607,394 discussed below.

US-A-3,607,394 is directed to a process for preparing a pregelatinized, cold water dispersible starch from a granular starch which contains at least 50% amylopectin (i.e., not more than 50% amylose). Suitable starches include cereal starches such as corn, wheat and barley, tuber starches such as potato and tapioca, and waxy starches such as waxy maize, waxy rice, and waxy sorghum. The high amylose starches, those which contain 60% or more amylose, as well as isolated amylose itself, are not suitable because their gelling characteristics are undesirable for the applications contemplated (i.e., where smooth pastes having a low initial viscosity and minimal setback). The process involves pasting at at least 149°C (300°F), with the upper limit being that at which substantial molecular degradation of the starch occurs, e.g., over about 232°C (450°F). The starch paste is then dried very rapidly in any suitable apparatus, e.g., a drum-dryer, spray-dryer, belt dryer, foam mat dryer or the like. The only requirement is that the apparatus be capable of drying the starch paste very rapidly to prevent retrogradation or aggregation prior to removal of the water. Also it is preferred that the paste be fed to the dryer very quickly because the longer it is held at a high temperature the greater is the likelihood of degradation. Structurally the products are characterized by complete granular fragmentation.

It is well known that high amylose starches are especially difficult to disperse and require higher temperatures and higher shear levels than low amylose starches such as corn, potato, wheat, rice, tapioca, and the like. Autoclaving or indirect heating, such as in a heat exchanger, are cooking processes that tend to produce dispersions that are complex colloidal mixtures, especially with the difficult to disperse high amylose starches. The mixtures consist of intact granules, residual granular fragments and dissolved polymer. Jet-cooking provides appropriate shear levels and more readily gives a dispersion approaching complete solubility at a molecular level (see US-A-2,805,966; US-A-2,582,198; US-A-2,919,214; US-A-2,940,876; US-A-3,133,836; and US-A-3,234,046. This more effective dispersion by jet-cooking provides a lower in-process viscosity, without degradation, than other cooking methods. This allows the use of lower cooking and conveying temperature and pressure which further assists in reducing degradation.

Therefore, there is a need for a spray-drying process which converts crystalline polymers to a substantially amorphous, i.e., "glassed" form, without substantial degradation by thoroughly cooking and drying water-dispersible or water-soluble natural polymers, such as unconverted starches and gums, or synthetic polymers such as polyvinyl alcohol at commercially acceptable solids concentration.

There is also a long felt need for a cooking and drying process that transforms cold-water-insoluble, partially insoluble, or slow to hydrate polymers (natural or synthetic) into new spray-dried powder forms which disperse in cold water and are substantially non-crystalline, non-retrograded and non-degraded by the process. The prior art teaches many

methods that produce pre-dispersed polymers, but the resulting polymers do not possess the full range of desired properties. There is a need for a spray-drying process which thoroughly cooks and dries crystalline polymers, such as converted starches, at higher solids than is currently possible.

In particular, there is a need for the following:

i) pregelatinized, spray-dried, fully pre-dispersed high amylose starches (modified or unmodified) which disperses in water (i.e., high amylose starches which are substantially cold-water-soluble and completely hot-water-soluble) and whose redispersions give strong gels with improved textural properties;

ii) fully pre-dispersed, spray-dried forms of modified or unmodified natural gums (which are inherently poorly dispersible due to crystalline or associated regions), especially polygalactomannan gums whose backbones are more linear in nature and have a tendency to associate to form crystalline regions, such as locust bean gum, and whose spray-dried forms yield cold-water redispersions with the solution properties of the parent gum.

iii) fully pre-dispersed, spray-dried forms of synthetic polymers which are inherently poorly dispersible due to crystalline or associated regions, especially substantially fully hydrolyzed polyvinyl alcohols and whose spray-dried forms yield cold-water redispersions with the solution properties of the parent polymer.

The coupled jet-cooking/spray-drying process described herein is a continuous process for jet-cooking and spray-drying an inherently water-dispersible or water-soluble polymer which is insoluble in cold water because of the presence of crystalline regions and which can be disoriented by heating, yielding a dispersion or solution which is low in viscosity at elevated temperatures. The process comprises the steps of:

(a) forming a slurry or a paste comprising the polymer and water;

(b) jet-cooking the aqueous slurry or paste of the polymer with steam at a temperature sufficient to fully disperse or solubilize the polymer;

(c) immediately conveying and introducing under elevated temperature and pressure the jet-cooked dispersion or solution into a nozzle of a spray-dryer chamber;

(d) atomizing the jet-cooked dispersion or solution through the nozzle of the spray-dryer;

(e) drying the atomized mist of the jet-cooked polymer within the spray-dryer chamber; and

(f) recovering the jet-cooked and spray-dried polymer as a water-dispersible or water-soluble powder.

The cooking temperature used will depend upon the polymer. The use of too high a cooking temperature may degrade a polymer such as starch. Suitable temperatures are about 93-177°C (200-350°F) for most polymers, 138-177°C (280-350°F) for starches containing about 70% amylose, 121-162°C (250-325°F) for starches containing less than about 40% amylose, 104-149°C (220-300°F) for low viscosity cold-water soluble starches, 99-163°C (210-325°F) for fully hydrolyzed polyvinyl alcohol and 93-163°C (200-325°F) for natural gums.

The cooking chamber pressure used in the continuous coupled process is low, typically $1.4\text{-}9.0 \cdot 10^5$ Nm^{-2} (20 to 130 psig), and is the saturation pressure of steam at the temperature used plus the small incremental pressure needed to move the dispersion through the chamber. Cooking chamber pressures suitable for high amylose starches are $5.5\text{-}10.3 \cdot 10^5$ Nm^{-2} (80 to 150 psig), most preferably $6.8\text{-}9.0 \cdot 10^5$ Nm^{-2} (100 to 130 psig) for a starch having an amylose content of about 70%.

Excessive shear, like too high a cooking temperature, will degrade a polymer such as starch and should be avoided unless a converted (i.e., degraded) starch is desired.

An essential step in the present process is the conveying of the thoroughly cooked, substantially fully dispersed polymer, under elevated pressure and temperature, to the spray-dryer atomization nozzle. In the preferred method, a low shear pneumatic nozzle is used, and the transfer is carried out at substantially the same temperature and pressure used in the jet-cooking. The transfer is carried out without any venting to the atmosphere. A pressure nozzle can be used for atomization. However, its use adds operational complexity to the process and may shear the dispersion, thus producing a degraded product.

One of the advantages of the coupled jet-cooking/spray-drying process is that it produces a fully pre-dispersed polymer, processed without substantial degradation and dried without substantial retrogradation or reassociation, which maximizes useful properties. The spray-dried powders redisperse in water to give dispersions with unexpected smooth textures and high viscosities or strong gel strengths.

Another advantage of the present continuous coupled process is that hydrolyzed starches having a water fluidity (W.F.) of about 80, which are conventionally spray-dried at 27% solids, are easily processed at 38% solids. Thus, the present process is limited only by the viscosity of the feed into the jet-cooker.

A further advantage of the present process is that low solids are not required for proper atomization of starches of higher viscosity. Prior art conventional processes with separated cooking and spray-drying steps are less advantageous when atomizable viscosities can only be obtained at low solids. In those two step processes, with 70% amylose starch, the cooled starch dispersion at atmospheric pressure is too viscous to spray-dry due to retrogradation or gel formation

if the solids content of the starch slurry is above 10% solids. In the continuous coupled, jet-cooking/spray-drying process the thoroughly cooked, hot dispersion is only slightly more viscous than water, even when the solids are 25%, and hence the dispersion can be easily spray-dried.

One disadvantage of cooking the starch slurry in a tubular heat exchanger, such as that used by Winkler in the examples of US-A-3,630,775 (discussed in the Background) is the higher temperature required since the slurry is indirectly heated rather than directly heated as with jet-cooking. The processing conditions used by Winkler in the high amylose starch example suggest that there were difficulties in dispersing the starch since the lowest percent solids, highest temperature and longest dwell time were used during cooking. Another disadvantage is the high pressure (above $6.9 \cdot 10^6$ Nm^{-2} (1000 psi)) required to transport the less than optimally dispersed starch through the heat exchanger and to atomize the dispersion using a single fluid pressure nozzle. A single fluid pressure nozzle is an extremely high shear atomization device which can cause molecular breakdown of high solids starch dispersions, hence altering viscosity and functionality. In contrast, in the continuous coupled jet-cooking/spray-drying process, the operating pressure when the preferred pneumatic nozzle is used is less than $10.3 \cdot 10^5$ Nm^{-2} (150 psig). Atomization is thus accomplished with less shear and minimum degradation results, thus maintaining viscosity or gelling properties of the original polymer. See Example XI which compares starches cooked in an heat exchanger and atomized through a single fluid pressure nozzle with starches cooked in a jet-cooker and atomized through a pneumatic nozzle.

All of the starches which are pregelatinized using the present process can be prepared in the form of fully predispersed, non-granular starches which are substantially non-crystalline (i.e., they are amorphous "glassed" solids). The jet-cooked dispersions are fully dispersed and do not contain granules or granular fragments; they are fully dispersed. Such pregelatinized starches are highly water-soluble and substantially non-degraded, i.e., the molecular weight of the processed starch is not substantially less than that of the unprocessed base starch. When the starch base is other than a high amylose starch, such as corn, tapioca, potato, waxy maize, and the like, the resulting pregelatinized starch powder is completely cold-water-soluble (CWS). When the starch base is a high amylose starch, the resulting pregelatinized starch powder is very soluble. For example, a hybrid corn starch having an amylose content of about 70% processed by the present process has cold and hot water solubilities of about 70% and 99%, respectively. These pregelatinized high amylose starch powders give high viscosity solutions when redispersed in hot water. The split second drying time during processing minimizes association through hydrogen bonding so that the resulting starches are substantially non-retrograded.

The unique spray-dried pregelatinized high amylose starches and their mixtures with other starches prepared by the present process form strong gels when redispersed in hot water (90-100°C - 194-212°F) and cooked in a boiling water bath for 15 minutes. The gel strength is about 230-240 g/cm^2 at 6% solids for a high amylose starch containing about 70% amylose, which is equivalent to the maximum gel strength obtained when the same starch is jet-cooked independently under optimum cooking conditions). Strong gels are also formed when these pregelatinized starches are redispersed in cold water (25°C - 77°F) and not cooked (150-160 g/cm^2 at 6% solids for a high amylose starch containing about 70% amylose). As is shown in Example XI, the starch is not degraded as is the starch pregelatinized using the process of US-A-3,630,775 (discussed in the Background). A spray-dried starch having an amylose content of about 70% which is pregelatinized using the present coupled process has an intrinsic viscosity between 0.7-0.9. The intrinsic viscosity of the non-processed base is typically between 0.9-1.0. This demonstrates that the present process produces a substantially non-degraded starch since the molecular weight of the processed starch is similar to that of the base starch from which it is derived.

Typical high amylose starches include those having an amylose content of about 100% (e.g., isolated potato amylose) or 40-70% (e.g., corn hybrids) and the starch may be modified by derivatization, conversion, or complexing. Modification by crosslinking is possible but not desirable as the advantage of the present process is the preparation of soluble starches. Lightly crosslinked starches that can be fully dispersed are suitable, whereas heavily crosslinked starches that are not fully dispersed during cooking are not suitable.

The starches prepared by the coupled process are amorphous white powders with particles having the shape typical of spray-dried starches, i.e. a convoluted indented sphere. However, unlike other conventionally spray-dried non-granular high amylose starches processed at low solids, the high amylose starch is substantially fully and completely disorganized as evidenced by amorphous X-ray patterns, substantially non-retrograded as evidenced by amorphous X-ray patterns and optimum gel strengths, and substantially non-degraded as evidenced by intrinsic viscosities that are similar to the base starch.

The high amylose starches prepared by the present coupled jet-cooking/spray-drying process are more completely dispersed than those prepared by the autoclaving and drum-drying process of US-A-3,086,890 (discussed in the Background). This is evidenced by the significantly higher gel strengths. For example, the pregelatinized starch having an amylose content of about 70% prepared by the continuous coupled jet-cooking/spray-drying process has a gel strength of about 160 g./cm.^{2} when redispersed in hot water at 6% solids, while the same base starch prepared by jet-cooking and drum-drying has a gel strength of only about 110 g./cm.^{2} when redispersed in hot water at 6% solids. This difference in gel strength is unexpected and an indication that the coupled continuous process produces a different product, i.e., a substantially fully disorganized and non-retrograded product. The autoclaving and drum-drying process of US-A-

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3,086,890 uses, as a starting material, a previously processed starch fraction (isolated amylose) which is prepared by high temperature cooking, precipitation of the desired fraction, and recovery by drying. In the present process, isolated starch fractions are usable, but native (non-cooked) starches are preferred.

The high amylose starch powders prepared by the coupled jet-cooking/spray-drying process are significantly more dense than pregelatinized starches prepared using a conventional two step process which involves jet-cooking and then spray-drying a low solids aqueous dispersion of the jet-cooked starch, as shown in Example XIII and discussed in Example XIV. The high amylose starch powders obtained herein also form a significantly firmer gel (about 200 versus 45-90 g./cm.^{2} at 6% solids when redispersed in hot water).

The high amylose starch powders and other starch powders prepared by the coupled jet-cooking/spray-drying process are completely non-granular unlike the pregelatinized starches prepared by cooking the starch in an atomized state. As described in US-A-4,280,851 (discussed in the Background), the simultaneously cooked and spray-dried starches are uniformly gelatinized granules in the form of indented spheres with a majority of the granules being whole and unbroken and swelling upon rehydration. In attempting to carry out this process with a high amylose starch (about 70% amylose), we have observed that it is difficult to prepare a highly soluble product. The high amylose starch is resistant to gelatinization under the processing conditions described in this reference.

Figure 1 shows the high temperature viscometer, a measurement device used to carry out the high-temperature flow rate viscosity measurement.

Figure 2 shows a X-ray crystallographic scan for a high amylose starch (about 70% amylose) pregelatinized by the present continuous coupled jet-cooking/spray-drying process (see Curve A), a high amylose starch (about 70% amylose) pregelatinized by jet-cooking and drying on a heated plate (see Curve B), and a high amylose starch (about 70% amylose) pregelatinized by jet-cooking and air-drying (see Curve C).

Figure 3 compares the gel strengths of spray-dried high amylose starches (about 70% amylose) pregelatinized using the present continuous, low shear, direct heating process which couples a jet-cooker with a spray-dryer having a pneumatic-type nozzle and the cook of the continuous, high shear, indirect heating process exemplified by US-A-3,630,775 which couples a tubular heat exchanger and a spray-dryer using a single fluid high pressure nozzle.

Figure 4 compares the viscosities of waxy corn starch, pregelatinized using the present continuous, low shear, direct heating process which couples a jet-cooker with a spray-dryer having a pneumatic-type nozzle, and the cook of the continuous, high shear, indirect heating process exemplified by US-A-3,630,775 which couples a tubular heat exchanger and a spray-dryer using a single fluid pressure nozzle.

Figure 5 compares the viscosities of corn starch pregelatinized using the present continuous, low shear, direct heating process which couples a jet-cooker with a spray-dryer having a pneumatic-type nozzle and the cook of the continuous, high shear, indirect heating process exemplified by

US-A-3,630,775 which couples a tubular heat exchanger and a spray-dryer using a single fluid high pressure nozzle.

Figure 6 presents scanning electron microscope photomicrographs of the fully dispersed, non-granular pregelatinized high amylose starch prepared by the continuous coupled jet-cooking/spray-drying process (see photograph A) with the granular, pregelatinized high amylose starch prepared by the simultaneous atomization and cooking process of US-A-4,280,851 (see photograph B) and with the pregelatinized high amylose starch prepared by the jet-cooking/drum-drying, a process similar to that of US-A-3,086,890 (see photograph C).

Figure 7 compares the displacement density and bulk density of various pregelatinized starches (potato amylose, high amylose corn, potato, corn, tapioca and waxy maize) prepared by the continuous coupled jet-cooking/spray-drying process, a conventional spray-drying process, and the jet-cooking/drum-drying, a process similar to that of US-A-3,086,890.

As used herein, the term "crystalline" polymer refers to any natural or synthetic polymer which contains crystalline regions or domains which must be disorganized to render the polymer amorphous and hence dispersible or soluble in cold water. Suitable polymers for use in the present process are those which develop a high viscosity after dispersion in hot water and whose aqueous dispersions have a reduced viscosity at elevated temperatures. Suitable natural polymers include water-dispersible or water-soluble polysaccharides such as starches, gums and cellulose derivatives. Suitable synthetic polymers include polymers such as fully hydrolyzed, medium to very high molecular weight polyvinyl alcohols.

Any cookable, granular unmodified or modified starch or previously cooked starch (including those not fully dispersed) other than a highly crosslinked starch is suitable as a starting material for use in the present process. Different types of suitable base starches include those from cereal grains, such as corn, milo, wheat and rice; those from tubers, such as potato, tapioca, and arrowroot; and those that are waxy starches, such as waxy milo, wavy maize, and waxy rice.

As used herein, the term "high amylose starch" refers to starches from any starch base which contain concentrations of at least about 40% amylose, including, for example, high amylose corn, wrinkled pea, and 100% amylose isolated from a starch such as potato starch. It also refers to mixtures of a high amylose starch and starches having an amylose content below 40%, such as waxy maize, corn, tapioca, potato, rice and the like. The mixtures can be processed and yield a mixed powder with good gelling properties, provided the mixture has a total amylose content of at least 35%. The preferred high amylose starches are those derived from high amylose corn hybrids.

Jet-cooking is a conventional process which involves the instantaneous heating of a flowing liquid (in the present process an aqueous suspension, also referred to as a slurry or paste) with a hot condensable vapor (in the present process steam) and holding the heated liquid at a selected temperature for a selected time. Various apparatus suitable for jet-cooking are referred to in the Background. Suitable cookers are available from National Starch and Chemical Corp. (United States), Avebe (Holland), or Roquette Freres (France).

Spray-drying is likewise a conventional process and described in Spray Drying: An Introduction to Principles, Operational Practice and Applications by K. Masters, published in 1972 by Leonard Hill Books, a division of International Textbook Co. Ltd., London. Spray-dryer nozzles suitable for use herein include pressure nozzles and pneumatic-type nozzles such as two-fluid nozzles.

In a pneumatic nozzle, the liquid to be atomized (here the cooked polymer dispersion) and an atomizing gas (air or steam) are fed separately to the nozzle at pressures generally between 3.4 and $13.7 \cdot 10^5$ Nm^{-2} (50 psig and 200 psig). Atomization is effected by impinging the pressurized atomizing gas on a stream of the liquid at a velocity sufficient to break the stream into droplets. In the present invention, pressure (and the resulting velocity) of the atomizing gas must be sufficient for proper atomization into small droplets to allow rapid drying to an appropriate residual moisture without retrogradation or reassociation. Use of pneumatic nozzles is preferred in the coupled jet-cooking/spray-drying process due to the low operating pressures (similar to those needed for jet-cooking) and the low shear on the feed inherent in this design. Pneumatic nozzles are discussed in greater detail on pages 16 f of Master's book cited above.

Pressure nozzles may also be used for atomization. Atomization, in a pressure nozzle, is effected by inducing rotation in the liquid and passing it through a small orifice. The liquid, on exiting the orifice, forms a cone-shaped film which is unstable, breaking into droplets. Use of a pressure nozzle in the present process requires insertion of a high pressure pump 1.4 to $6.9 \cdot 10^7$ Nm^{-2} (2,000 to 10,000 psig) between the jet-cooker and the atomization nozzle. The temperature after passage through the high pressure pump should be maintained substantially equivalent to the jet-cooking chamber temperature. The pressure after the high pressure pump must be sufficient to properly atomize the dispersion into small droplets to allow rapid drying to an appropriate residual moisture without retrogradation or reassociation. Use of a pressure nozzle adds operational complexity to the present process and may shear the dispersion, thus producing a degraded product. Suitable pressure nozzles are also described in the Masters reference cited above.

For example, in the present process a starch slurry (up to 38% anhydrous basis) is prepared. The starch slurry is then directed through a cooking chamber, mixed with high temperature steam (at $5.5\text{-}10.3 \cdot 10^5$ Nm^{-2} 80-150 psig), and gelatinized in a continuous jet-cooker. The starch is cooked at a solids and temperature sufficient to reduce its viscosity at elevated temperature to a low range (near that of water), without significant degradation.

The exit of the cooking chamber is connected to a spray-nozzle, preferably a pneumatic-type spray-nozzle, situated in a spray-dryer. The starch cook, while still at a high temperature and low viscosity, is directed into the spray-nozzle and atomized with cold air, hot air or steam. Once the hot jet-cook has been atomized, it is handled in the same manner as conventional spray-dried starches.

The continuous coupled process is economical. It provides high flow rates through a given spray-dryer orifice at high starch solids but at pressures that are low enough to minimize degradation of the starch.

The coupled process is versatile. The processing equipment may be arranged to optionally add other materials during the jet-cooking step. For example, (1) a water-soluble compound such as sugar or a water-dispersible compound such as a gum can be added to a starch slurry and a spray-dried mixed powder obtained; (2) a water-insoluble compound, such as an oil, can be added to the starch and a starch powder containing encapsulated oil obtained; (3) a complexing agent such as a surfactant can be added to a starch slurry and a starch-surfactant complex obtained; (4) an acid may be added to the slurry and an acid-converted starch product obtained; or (5) a derivatizing agent may be added to the slurry and a derivatized starch product obtained. The processing equipment can also be arranged to provide for post-drying treatments such as the agglomeration of the starch powder, or a heat-moisture treatment of the starch powder.

The above procedure (encapsulation, complexation, conversion, derivatization, agglomeration, and heat treatment) are well-known starch modifications and described, for example, in Chapter 22: Starch and Its Modification by M.W. Rutenberg in Handbook of Water-Soluble Gums and Resins, edited by Robert L. Davidson and published by McGraw Hill Book Co., New York 1980 or in the patent literature.

Jet-cooks of a high amylose starch (about 70% amylose) maintained at temperatures from 126-153°C (259-307°F) flow through spray-drying nozzles at rates no less than half that of water, even at a 28% cook solids. This translates into a flow viscosity of less than 1 centipoise at temperatures of 109-145°C (228-293°F). The viscosity of a 28% solids jet-cook of the same starch cannot be measured after it exits the cooker and drops in temperature to below 100°C (212°F) since it forms a gel in a few seconds. Therefore, flow rates are measured instead of viscosity. Accurate viscosity measurements of non-Newtonian liquids such as starch cooks are very difficult to measure.

Starch cook viscosities (by flow rate comparison with water) decrease with increasing temperature, decreasing molecular weight, decreasing solids, and increasing amylose content (e.g., a high amylose starch having an amylose content of about 50% is more viscous than a high amylose starch having an amylose content of about 70%).

In the examples which follow, all temperatures are in degrees Celsuis and Fahrenheit. All spray-drying nozzles are obtainable from Spray Systems Co., Wheaton, Illinois. The following test procedures were used.

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Water Solubility

A. Cold Water Solubility

The determination is carried out using distilled water at room temperature. About 0.5 g. of starch is dispersed in 30-40 ml. of water in a semi-micro stainless steel cup on a Waring blender base (Model 31B292). The blender is run at low speed while the starch is added (all at once) and then run at high speed for 2 minutes. The dispersion is immediately transferred to a 50 ml. volumetric flask and diluted to 50 ml. with water. A 25 ml. portion of the stock dispersion (shaken well to ensure a homogenous dispersion) is removed by pipet and transferred to a 50 ml. centrifuge tube. The sample is spun down at 1800-2000 RPM for 15 minutes. Once spun down, 12.5 ml. of supernatant is pipetted into a 25 ml. volumetric flask, 5 ml. of 5 N potassium hydroxide (KOH) are added with swirling, and the mixture is diluted with water. The remainder of the stock dispersion is shaken well, the insoluble starch dispersed with 10 ml. of 5 N KOH while swirling. The mixture is diluted to 50 ml. with water. The optical rotation of both the concentrated stock solution (B) and the supernatant solution (A) is measured.

$$\% \text{ Cold Water Solubles} = \frac{\text{Optical Rotation of Supernatant/Path Length of Supernatant}}{\text{Optical Rotation of Stock Solution/Path Length of Stock Solution}} \times 100$$

B. Hot Water Solubility

The procedure is the same as that described above except that boiling distilled water at 90-100°C (194-212°F) is used for dispersing the starch and all subsequent dilutions. No attempt is made to maintain temperature during the procedure.

Fluidity Measurements

A. Water Fluidity (W.F.)

This test is described in US-A-4,207,355, the disclosure of which is incorporated herein by reference.

B. Calcium Chloride Viscosity (7.2% Solids Test)

The calcium chloride viscosity of the converted high amylose starch is measured using a Thomas Rotation Shear-Type Viscometer standardized at 30°C. (86°F) with a standard oil having a viscosity of 24.73 mPas (cps)., which oil requires 23.12 ± 0.05 seconds for 100 revolutions. As the conversion of the starch increases, the viscosity of the starch decreases and the calcium chloride viscosity decreases. Accurate and reproducible measurements of the calcium chloride viscosity are obtained by determining the time which elapses for 100 revolutions at a specific solids level.

A total of 7.2 g. of the converted starch (anhydrous basis) is slurried in 100 g. of buffered 20% calcium chloride solution in a covered semi-micro stainless steel cup (250 ml. capacity available from Eberbach), and the slurry is transferred to a glass beaker and is heated in a boiling water bath for 30 minutes with occasional stirring. The starch solution is then brought to the final weight (107.2 g.) with hot (approximately 90-100°C - 194-212°F) distilled water. The time required for 100 revolutions of the resultant solution at 81-83°C. (178-181°F) is measured three times in rapid succession and the average of the three measurements is recorded.

The calcium chloride solution is prepared by dissolving 264.8 g. of reagent grade calcium chloride dihydrate in 650 ml. of distilled water in a tared 1 l. glass beaker. Thereafter 7.2 g. of anhydrous sodium acetate is dissolved in the solution. The solution is allowed to cool and the pH is measured. If necessary, the solution is adjusted with hydrochloric acid to pH 5.6 ± 0.1. The solution is then brought to weight (1007.2 g.) with distilled water.

Gel Strength

A gel is prepared by dispersing a starch sample (on an anhydrous basis) in boiling distilled water (approximately 90-100°C - 194-212°F) at appropriate solids in a Waring blender (Model 31B292) set at low speed for 2 minutes, transferring to a glass beaker, then cooking the sample in a boiling water bath for 15 minutes. The sample is brought back to weight with boiling distilled water and is then placed in a jar covered with a lid and allowed to cool undisturbed for 24 hours at 21°C (70°F) to gel. Unless stated otherwise, all gels are prepared in boiling water and cooked as stated above. For cold water gel strengths, the gel is made in room temperature (25°C - 77°F) distilled water without cooking. The strength is measured using a Stevens LFRA Texture Analyzer (available through Texture Technologies Corp., Scarsdale, NY) employing a 0.64 cm (0.25) in. diameter cylindrical probe, run at a speed of 0.5 mm./sec. The force in g./cm.^{2} required for the probe to penetrate the gel a distance of 4 mm. is measured three times and the average is recorded. The solids and probe selection are varied according to the starch type. For example, all high amylose corn starches

(about 70% amylose) and isolated potato amylose (about 100% amylose) were tested with a 0.25 in. diameter cylindrical probe at 6% solids (dry basis). Unless stated otherwise, these conditions can be assumed.

Brookfield Viscosity

Brookfield viscosity is measured using a RVF Brookfield viscometer (available through Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts) and an appropriate spindle at 20 rpm. The instrument is allowed to rotate five times before a reading is taken. All viscosity readings are run at 22°C (72°F), and all test dispersions are prepared using the above gel strength procedure unless stated otherwise.

Intrinsic Viscosity Determination

The intrinsic viscosity of starch is measured by quantitatively transferring 2.500 g. ± 0.001 g. of anhydrous starch into a 600 ml. beaker containing about 250 ml. of distilled water at about 25°C (77°F). Then 100 ml. of 5N ± 0.05N KOH solution are pipetted into the beaker, and the mixture is stirred for 30 minutes on a stir plate. This solution is clear and does not contain undissolved starch. The solution is quantitatively transferred to a 500 ml. volumetric flask and is brought to volume with distilled water. The solution is filtered through a funnel packed with glass wool. Then 40.0, 30.0, 20.0 and 10.0 ml. of this solution are pipetted into 50 ml. volumetric flasks and brought to volume with 1N ± 0.10 N KOH solution. The flow times for each concentration (0.40, 0.30, 0.20 and 0.10% solids plus the stock solution at 0.50% solids) and the flow time of the 1 N KOH solution is determined in a Cannon-Fenske Viscometer (No. 100, 45-65 seconds flow time for water at 35°C) mounted in a constant temperature bath maintained at 35.00 ± 0.02°C. The flow times for each dilution are run in triplicate. The intrinsic viscosity is the point at which the extrapolated line of a plot of N_{sp}/concentration (y-axis) versus concentration (x-axis) intercepts the y-axis. $N_{sp} = N_{rel} - 1$ and

$$N_{rel} = \frac{\text{flow time of starch solution}}{\text{flow time of 1 N KOH}} .$$

Viscosity by Flow-Rate Measurement

The device used for high-temperature flow-rate viscosity measurement is shown in Figure 1. It is used to measure the flow rate of fluids under high temperature/pressure conditions. A jet-cooker is used to raise the temperature/pressure of these fluids. The high temperature starch cook viscosity is determined by comparing its flow rate to that of water under identical conditions. Solids concentration are stated in the Examples.

The "small" nozzle orifice, which has an opening of 0.04 cm (0.016 in.), is used for low solids cooks (spraying systems fluid cap 40100). The "large" nozzle orifice, which has an opening of 0.079 cm (0.031 in.), is used for high solids cooks (fluid cap 600100).

A. Cooked Starch Flow Rate Measurement

The starch is slurried in water at the desired solids and adjusted to approximately pH 6 with dilute sulfuric acid or sodium hydroxide as required. The slurry is then jet-cooked at temperatures between 149-155°C (300-311°F). The starch cook is then directed (while kept at temperature) into an insulated steel chamber fitted with a spray-drying nozzle and an overflow line to flash off excess steam and to control pressure. The valve opening to the overflow line is adjusted to bring the pressure and thus the temperature to the desired point and to eliminate any excess steam. Gases (steam) in the liquid stream cause an uneven flow ("spitting") and must be eliminated to provide accurate flow results. Once the pressure/temperature have been adjusted and steam has been eliminated, a valve is opened to allow flow through the spray-drying orifice while maintaining constant pressure. Simultaneously, a graduated cylinder is placed under the orifice and a timer is started. A sample is collected for approximately 30 seconds, from which the flow rate per minute is calculated. Water is run through this procedure and is used as the standard for comparison.

B. Water Flow Rate Measurement

Water was run at $1.4 \cdot 10^5$, $2.8 \cdot 10^5$ and $4.1 \cdot 10^5$ Nm^{-2} (20, 40 and 60 psig) of pressure to obtain temperatures of 126°, 142°, and 153°C (259°, 287°, 307°F) using the procedure given above. The results are shown below:

Orifice Size Cm (in.)	Pressure Nm^{-2}(psig)	Temperature of Fluid °C (°F)	Flow Rate (ml./minute)
0.04 (0.016)	$1.4 \cdot 10^5$ (20)	126 (259)	100
0.04 (0.016)	$2.8 \cdot 10^5$ (40)	142 (287)	138
0.04 (0.016)	$4.1 \cdot 10^5$ (60)	153 (307)	180
0.079 (0.031)	$1.4 \cdot 10^5$ (20)	126 (259)	360
0.079 (0.031)	$2.8 \cdot 10^5$ (40)	142 (287)	600
0.079 (0.031)	$4.1 \cdot 10^5$ (60)	153 (307)	699

Powder Density

A. Bulk Density

A tared 100 cc. graduated cylinder is filled to the 100 cc. mark with "as is" test sample powder. The cylinder is tapped on a hard surface until no further drop in volume is noted.

$$\text{Bulk Density} = \frac{\text{g. of starch}}{\text{cc. of packed volume}} \; (\times 62.427 = \text{lbs./ft.}^3)$$

B. Displacement Density

A Hubbard-Carmick, 25 ml. capacity, specific gravity bottle is tared and a small amount of anhydrous glycerin is added to wet out the bottom of the bottle. A known amount of starch (about 5 g. "as is") is weighed into the bottle and the bottle is filled about half way with more glycerin. After mixing, the bottle is filled within 0.64 to 0.32 cm (1/4 to 1/8 inch) of the top with glycerin and placed under a vacuum until all air bubbles are dissipated. Glycerine is added to completely fill the bottle and the total weight is taken. The procedure is run with glycerin alone (no starch) to determine the volume of the bottle. All work must be done at 25°C (77°F).

$$\text{Volume of Bottle} = \frac{\text{Weight of glycerin (no starch)}}{\text{Specific Gravity of glycerin}}$$

$$\text{Volume of Glycerin} = \frac{\text{Weight of glycerin (with starch)}}{\text{Specific Gravity of glycerin}}$$

$$\text{Volume of Starch} = \text{Volume of bottle-Volume of glycerin}$$

$$\text{Displacement Density} = \frac{\text{Weight of Starch}}{\text{Volume of Starch}} = \text{g./cc.}$$

Example I

This example shows the preparation of pregelatinized non-granular high amylose corn starches (about 70% amylose).

Part A - Preparation at Lower Cook Solids (13%)

An unmodified granular high amylose starch was slurried in water and pumped using a gear pump into a jet-cooker. Steam (at $10 \cdot 10^5$ Nm^{-2} (145 psig)) was metered into the slurry stream and the starch was cooked. The hot starch cook was conveyed at a temperature and pressure only slightly reduced from the cooking chamber to a pneumatic atomization nozzle bottom mounted in a spray-dryer. Compressed air was used to atomize the starch. Hot air in counter-current flow

was used to dry the atomized starch mist. The resulting powders were recovered in a cyclone separator. The process variables used are shown in Table I. The spray-dryer is a laboratory Model No. 1 Anhydro spray-dryer.

The effect of cooking shear on the gel strength of starch powders redispersed at 6% solids in hot water is shown. The shear was varied by varying the amount of gaseous steam present in the starch cook as it moved through the cooker. At lower shear levels (20.0 g./min. of steam flow), the starch was not thoroughly and efficiently cooked, and this was reflected in less than maximum gel strength (194 g./cm.^{2}) (see Column 1). At optimum shear levels for this system (24.0 g./min. steam flow) a maximum gel strength of 215 g./cm.^{2} was achieved. Increasing the shear by using a steam flow of 36 or 62 g./min. resulted in lower gel strengths (204 and 134 g/cm.^{2}) (see columns 3 and 4). Proper shear must be determined experimentally and it will depend on the starch used, the hydraulic characteristics of the cooking and atomizing equipment used, and the cooking temperature, as well as the gel strength required for the desired end use.

Part B - Preparation at Higher Cook Solids (28%)

The process variables used for jet-cooking/spray-drying in larger scale equipment at higher solids are shown in Column 5 of Table 1. The slurry of unmodified granular high amylose starch was fed into a jet-cooker (Model C-15 available from National Starch and Chemical Corp). Steam was metered into the slurry as above. The cooked starch was conveyed to a pneumatic atomization nozzle top mounted in a 1067 cm (35 ft.) tall, 488 cm (16 ft.) diameter Hensey spray-dryer. Steam at $8.3 \cdot 10^5$ Nm^{-2} (120 psig) was used to atomize the starch. The atomized starch mist was dried with air at 204°C (400°F).

The cold water solubility of the above non-granular starch powders was 97.4% and the hot water solubility was greater than 99%.

The types of pneumatic nozzle set-ups used in the spray-dryers are indicated in the Table and available from Spraying System Inc.

Example II

This example demonstrates the processing of a converted high amylose corn starch (about 70% amylose) using the coupled jet-cooking/spray-drying process. A slurry of the starch was treated with 2.5% hydrochloric acid at 52°C (126°F) for 16 hours to give a converted starch having a calcium chloride viscosity of 25 seconds. After neutralization with sodium carbonate to a pH of about 6, the granular converted starch was filtered, washed and dried. The starch was then jet-cooked using the following conditions: 21% cook solids, 143°C (290°F) cooking temperature, 27 g./min. steam flow, and 39.7 ml./min. cooking rate. The jet-cooked starch dispersion was spray-dried through a two fluid Spray Systems nozzle (set-up 22) into a Niro Utility #1 spray-dryer. The inlet temperature was 250°C (428°F) and the outlet temperature was 88°C (190°F). The starch powder was 93.0% soluble in cold-water and 97.1% soluble in hot-water.

Example III

This example demonstrates that a blend of a high amylose corn starch and another starch can be processed using the coupled jet-cooking/spray-drying process. About 35 parts of a converted high amylose corn starch (about 70% amylose and calcium chloride viscosity of about 25 seconds) was slurried with about 65 parts of a converted corn starch (about 28% amylose and water fluidity of 65) in 150 parts of water. The following jet-cooking conditions were used: 23% cook solids, 143°C (290°F) cooking temperature, 27.5 g./min. steam flow, and 39 ml./min. cooking rate. The jet-cooked starch dispersion was spray-dried through a two-fluid Spray Systems nozzle (set-up 22B) into an Anhydro laboratory Model No. 1 spray-dryer. The inlet temperature was 230°C (446°F) and the outlet temperature was 86°C (187°F).

The resulting non-granular starch powder was 95.1% soluble in cold water and greater than 99% soluble in hot water. On redispersion in hot water at 6% solids it formed a gel having a strength of 42 g./cm.^{2}. The fluidity corn starch processed under similar conditions did not gel. The fluidity high amylose corn starch processed under similar conditions formed a gel having a strength of 75-85 gm./cm.^{2}. The results show that the co-processed blend provided a starch powder which formed a gel.

Example IV

This example demonstrates that a mixture of a granular unmodified high amylose corn starch (about 70% amylose) and fructose or sorbitol can be processed using the coupled jet-cooking/spray-drying process.

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The processing conditions and results were as follows:

Conditions	Typical High Amylose Starch (Comparative)	87.5% High Amylose Starch + 12.5% Fructose	92.5% High Amylose Starch + 7.5% Sorbitol
Cook solids (%)	15-16	14.5	14.0
Cooking temperature (°C(°F))	143(290)	143(290)	143(290)
Steam flow (g./min.)	27.5	27.5	27.5
Cooking rate (ml./min.)	24-36	35.0	35.0
Spray-dryer	Anhydro	Anhydro	Anhydro
Inlet temperature (°C(°F))	240(464)	220(428)	230(446)
Outlet temperature (°C(°F))	90(194)	82(180)	84(183)
Two fluid nozzle set-up	22B	22B	22B
Cold water solubility (%)	71.4	64.9	96.6
Hot water solubility (%)	94.5	83.7	80.3
Gel strength at 6% solids (g./cm.^{2})	220	119.0	172.0

The results show that co-processed powdered mixtures were highly soluble (64.9 and 96.6%) in cold water and formed strong gels (119 and 172 g./cm.^{2}) even though they contained lower starch solids than the comparative sample.

Example V

This example describes the production and recovery of a derivatized starch using the coupled jet-cooking/spray-drying process.

A starch is slurried in water and the pH is adjusted to between pH 6 and pH 8 with sulfuric acid or sodium hydroxide as required. An aqueous sodium tripolyphosphate (STP) solution is added either to the bulk starch slurry or metered into the starch feed line prior to the jet-cooker at a level sufficient to give 1 to 4% STP on starch. The starch/STP slurry is jet-cooked at a temperature 163-177°C (325-350°F).

This modified starch dispersion is conveyed, at temperature and pressure substantially equivalent to those used during cooking directly to an atomization nozzle mounted in a spray-dryer. After atomization and drying the resulting powder is collected.

It is expected that the recovered starch powder will have the properties of a conventional starch phosphate produced by slurry reaction. In addition, it is expected that the powder will be readily water-soluble and not require cooking to produce a functional water dispersion. Reactions on cooked starches are known but yield liquid products and have generally been avoided due to difficulty in recovering the viscous reaction products or expense in recovering low solids cooks. For example, US-A-3,637,656 and US-A-4,579,944 describe paste reaction processes for making starch derivatives.

Example VI

This example shows that other granular high amylose corn starches can be jet-cooked and spray-dried using the coupled process. The processing conditions used for fractionated potato amylose (about 100% amylose), unmodified high amylose corn starch (about 50% amylose), and converted high amylose corn starch (about 70% amylose and having a calcium chloride viscosity of 25 seconds) are shown in Table II.

The results show that the non-granular powders are highly soluble in cold water (86.6, 95.3, and 93.0%, respectively) as well as in hot water (99.2, 96.9, and 97.1%). They form strong gels (395, 125 and 104 g/cm^2, respectively).

Example VII

This example demonstrates the use of the coupled jet-cooking/spray-drying process to prepare a cold-water-soluble form of a cold-water insensitive synthetic polymer.

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A medium molecular weight fully hydrolyzed polyvinyl alcohol (available from E. I. DuPont de Nemours under the trade name Elvanol 71-30) was slurried in water at 3% solids and jet-cooked at 143°F (290°F). Back pressure at the cooking chamber was $3.8 \cdot 10^5$ Nm ^{2} (55 psig). The dispersed polymer was conveyed under pressure $3.1 \cdot 10^5$ Nm ^{2} (45 psig) through an atomization nozzle (Model 1/2 J82 available from Spraying Systems Inc.) top mounted in a Niro Utility #1 spray-dryer and atomized with steam at $2.1 \cdot 10^5$ Nm^{-2} (30 psig). Heated air at 280°C (536°F) was used to dry the atomized solution to a free flowing powder.

The resulting product consisted of rugose spheres generally from 3 to 6 microns in diameter. A total of 31.88% of this material was soluble in water at 25°C (77°F) compared to 3.6% of the unprocessed polymer. The solubility test used is the one described in 4,072,535. DuPont's technical service bulletin issued December 1965 describes the PVA polymer as having "excellent resistance to cold water" and requiring elevation to 90-95°C (194-203°F) for complete dissolution in water. The viscosity of the spray-dried polymer at 25°C (77°F), dispersed in hot water at 4% solids, was 24 mPas (cps.) compared to 26 mPas (cps.) for the unprocessed polymer. This shows that the polymer was not substantially degraded during the processing.

Example VIII

This example illustrates the use of the coupled jet-cooking/spray-drying process to produce a cold-water-soluble powder from a polygalactomannan gum which is normally difficult to solubilize.

Locust bean gum (available from National Starch Chemical Corp.) was slurried in water at 1% solids and jet-cooked at 132°C (270°F). Back pressure at the cooking chamber was $2.1 \cdot 10^5$ Nm^{-2} (30 psig). The dispersed gum was conveyed under pressure (25 psig) through an atomization nozzle (Model 1/2 J82) top mounted in a Niro Utility #1 spray-dryer and atomized with steam at $2.1 \cdot 10^5$ Nm^{-2} (30 psig). Heated air at 280°C (536°F) was used to dry the atomized mist to a free flowing powder.

The resulting product consisted of rugose spheres generally from 2 to 4 microns in diameter. A total of 71.5% of this powdered gum was soluble in water at 25°C (77°F) compared to 27.1% of the unprocessed gum. When redispersed in cold water at 4% solids, the viscosity was 490 mPas (cps.) within 2 minutes compared to 16 mPas (cps.) for the unprocessed gum. The solubility test referred to in Example VII was used.

Example IX

This example describes the processing conditions used in the continuous coupled jet-cooking/spray-drying process when starches other than high amylose starches are pregelatinized. The equipment used is described in Example I. The processing variables and results are shown in Table III.

The results show that the non-granular corn, waxy maize, and tapioca starch powders were essentially 100% cold-water-soluble.

Example X

This example compares the flow viscosity of jet-cooked high amylose corn starch (about 70% amylose) to water at elevated temperatures. High amylose starch slurries were cooked at solids of about 16.8-18.1%, cooking temperature of about 149°C (300°F), steam flow rate of 168 g./min., and cooking rate of 59.3 ml./min. The resulting flow rates through the viscometer previously described were 48, 91 and 113 ml./min. at 1.4, 2.8 and $4.1 \cdot 10^5$ Nm^{-2} (20, 40 and 60 psig) of pressure using a 0.04 cm (0.016 in.) orifice in the atomizer nozzle. For a 0.079 cm (0.031 in.) orifice, the resulting flow rates were 313-498 and 399-642 ml./min. at 2.8 and $4.1 \cdot 10^5$ Nm^{-2} (40 and 60 psig). Flow rates of water, under identical conditions were 100, 138, 190, 600 and 699 ml./min., respectively.

It can be seen that jet-cooks of high amylose corn starch flow through the spray-drying nozzles at rates no less than half that of water when the temperatures were maintained at from 126 to 153°C (259 to 307°F) even at 28% cook solids. This translates into a flow viscosity of less than 1 centipoise.

In contrast, when the temperature drops after a 28% solids jet-cook of high amylose corn starch exits the jet-cooker, the viscosity cannot even be measured as the starch cook forms a gel in a few seconds.

Example XI

This example compares starches pregelatinized using the continuous coupled, jet-cooking/spray-drying process with the same starches pregelatinized using the process of US-A-3,630,775.

The procedure of the patent could not be exactly duplicated. The spraying pressures disclosed in the patent range from $1.4 \cdot 10^7$ to $4.7 \cdot 10^7$ Nm^{-2} (2000 to 6800 psig) and the cooking temperatures range from 182-304°C (360-580°F). The equipment used for this experiment was limited to a pressure of $1.1 \cdot 10^7$ Nm^{-2} (1600 psig) and a temperature of 160°C (320°F).

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A B.I.F. (a division of New York Air Brake, Providence, Rhode Island) model 1180 jacketed micro-feeder piston pump was modified to produce higher flow rates so that pressures up to $1.1 \cdot 10^7$ Nm^{-2} (1600 psig) could be achieved. Thermocouples were attached to the cooking chamber to monitor the temperature of the cook. The piston cavity was filled with starch slurries at 10% to 20% solids. The slurries were heated for 20 minutes to a temperature of 160°C (320°F) with $6.9 \cdot 10^5$ Nm^{-2} (100 psig) of steam flowing through the jacket of the pump. The starch was then pumped through a single fluid nozzle having a 0.0343 cm (0.0135 in.) orifice (#80A available from Spraying Systems Inc.) at $1.1 \cdot 10^7$ Nm^{-2} 1600 psig pressure. Samples were collected and analyzed for viscosity or gel strength.

Part A - High Amylose Starch (70% amylose)

Comparative starch samples were sprayed at $1.1 \cdot 10^7$ Nm^{-2} (1600 psig) and 160°C (320°F), collected, and allowed to cool and set-up for 24 h at 21°C (72°F).

Gel strengths were run on the Texture Analyzer. Cook solids were run (using an infra-red heat lamp balance) after the gel strengths were tested.

The jet-cooking conditions used to prepare the pregelatinized starch by the coupled process were as follows: 28% cook solids (38% slurry solids), steam flow of 31 g./min., cooking temperature of 143°C (290°F), flow rate of 38.7 ml./min., and back pressure of $3.59 \cdot 10^5$ Nm^{-2} (52 psig) at the chamber and $3.31 \cdot 10^5$ Nm^{-2} (48 psig) at the nozzle. The spray-dryer used was an Anhydro Dryer Model No. 1 equipped with a two fluid nozzle (set-up #22B). The inlet temperature of the spray-dryer was 230°C (446°F) the outlet temperature was 84°C (183°F) and air at $1.4 \cdot 10^5$ Nm^{-2} (20 psig) was used for atomization.

The starches were dispersed in hot water and heated in a boiling water bath for 15 minutes, allowed to cool and set-up for 24 hours at 21°C (72°F). The solids and gel strengths are shown below. The starch degradation is shown in Figure 3.

Sample	Solids (%)	Gel Strength (g./cm.^{2})
Indirect cooking/spraying (comparative)	11.1	370
	13.4	580
Continuous coupled jet-cooking/spray-drying process	10.3	557
	13.4	768
	13.8	946
	16.6	+996*

* Gel strengths over 950 g are not accurate, as they are over the upper limits of the Texture Analyzer.

The results show that the high amylose starches prepared by indirect heating and pressure atomization gave lower gel strengths than the same starch cooked and atomized by the coupled process using direct heating. This is attributed to the less effective dispersion formed during indirect heating and the higher shear developed during atomization in the pressure nozzle. It would be expected that pressures and temperatures exceeding those used here, as taught in Winkler, will only further degrade the starch.

Part B - Other Starches

Comparative starch samples of waxy maize starch (about 0% amylose) and corn starch (about 28% amylose) were sprayed at $1.1 \cdot 10^7$ Nm^{-2} (1600 psig) at a temperature of 160°C (320°F) and allowed to cool to 71°C (160°F) before viscosity measurements were taken.

Waxy maize and corn starch samples pregelatinized using the coupled process were spray-dried at inlet temperatures of 200°C (392°F) and 200°C (392°F), and outlet temperatures of 125°C (257°F) and 82°C (180°F), using $2.1 \cdot 10^5$ Nm^{-2} (30 psig) of atomization steam and $2.1 \cdot 10^5$ Nm^{-2} (30 psig) of atomization air, respectively. The spray-dryer used for the waxy maize starch was a Niro Utility #1 dryer equipped with a two fluid nozzle (set-up 22B nozzle and 120 cap). That used for the corn starch was an Anhydro Model No. 1 dryer with the same nozzle and set-up.

The recovered starches were dispersed in hot water and heated in a boiling water bath for 30 minutes and allowed to cool to 71°C (160°F) before viscosity measurements were taken. Cook solids were run (using an infra-red heat lamp balance) after all samples had been tested. The solids and viscosities are shown below. The gel strengths are given in

Part A.

Sample	Solids (%)	Viscosity mPas (cps)
Waxy Maize prepared by continuous coupled jet-cooking/spray-drying process	11.9	423
	15.6	740
	20.0	1850
Waxy Maize prepared by indirect cooking/spraying (comparative)	10.0	30
	14.0	37
	19.4	190
	21.2	340
Corn prepared by continuous coupled jet-cooking/spray-drying process	12.0	620
	16.3	3650
	20.4	24500
Corn prepared by indirect cooking/spraying (comparative)	12.0	28
	14.0	37
	19.4	190

The results again show that high molecular weight starches, such as native waxy maize and corn starch, were degraded, as shown by the extreme reduction in viscosity, when processed using indirect heating and a pressure nozzle. The starch degradation is shown in Figures 4 and 5.

Example XII

This example demonstrates that the pregelatinized, spray-dried, non-granular, amorphous high amylose starches prepared by the coupled process are unique. X-ray crystallographic scans (see Figure 2) performed by Rigaku USA Danvers Mass Model No. DMAX-8 showed that the pregelatinized high amylose starch (about 70% amylose) prepared by the coupled jet-cooking/spray-drying process was amorphous, i.e., there were no crystalline peaks. Comparative pregelatinized starches (about 70% amylose) prepared by jet-cooking followed by drying on a heated plate unexpectedly contained crystalline regions. Samples made by jet-cooking followed by air-drying contained crystalline regions as expected. Native granular starch likewise contains crystalline regions.

The lack of retrogradation in the coupled jet-cooked/spray-dried material is confirmed by the higher gel strength on redispersion (160 g./cm.^{2} at 6% solids in hot water). The same high amylose starch processed by jet-cooking and drum-drying had a gel strength of only 110g./cm.^{2} on redispersion.

It is well known that retrograded starches do not provide as strong a gel on redispersion below 100°C (212°F) compared to a more soluble starch of equal amylose content. This is due to the unavailability of the retrograded amylose for gel formation.

Example XIII

Scanning Electron Microscopa photomicrographs of pregelatinized high amylose (about 70% amylose) corn starches prepared by the present coupled jet-cooking/spray-drying process (Photograph A), the simultaneous atomization and cooking process of US-A-4,280,851 (Photograph B), and the autoclaving/drum-drying process of US-A-3,086,890 (Photograph C) are shown in Figure 6. The photomicrographs of the particles that make up the powders of these starches show distinct physical differences.

The powders of the current invention are composed of non-granular, round, spray-dried particles having convoluted (dimpled) surfaces due to the rapid removal of water and subsequent collapse of the starch-film during drying. In this process, the size of the particles are determined by the size of the droplets formed during atomization and drying. These particles are unlike those prepared by the simultaneous atomization and cooking process which are generally in the form of swollen granules. This is evidenced by the slightly wrinkled surfaces characteristic of intact, swollen starch granules. Though a spray-dried particle, the starch in this photomicrograph (photograph B) was never placed into solution

and the particle size is determined largely by the degree of granular swelling during cooking. The powders of the autoclaving/drum-drying process are in the form of angular flakes. The particle size is determined by subsequent grinding and fractionation of the drum-dried sheet after drying.

The preparation of a spray-dried high amylose starch by the process of US-A-4,250,851 was difficult, and the resulting product was considerably less soluble and contained intact, non-degraded granules. As previously shown, the preparation of such a starch by the coupled process was easily carried out.

Example XIV

This example compares the displacement density and bulk density of various pregelatinized starches prepared by the present coupled jet-cooking/spray-drying process at high solids, a conventional spray-drying process at low solids, and the jet-cooking/drum-drying process similar to that of US-A-3,086,890 at low solids. The starches prepared by the coupled process were prepared using suitable processing conditions for the particular starch source.

The results in Figure 7 show that the relationship between displacement density and bulk density for the various methods of preparing pregelatinized starches are specific and generally lie within regions that are independent of the starch source. These density differences are due to the differences in particle shape and structure resulting from the drying step of each process.

Particles produced by the process of US-A-3 086 890 are flakes which contain loss included air than starch powders spray-dried from dispersions; thus, the density of the individual particle of the process of US-A-3 086 890 (i.e., displacement density) is higher than that of spray-dried starch powders from dispersions. However, these angular flakes pack together less efficiently than spheres giving a lower bulk density.

Spray-dried starch particles dried from a dispersion generally are characterized by internal air voids and surface ridges and depressions. This structure is formed, in the spray-dryer, as the wet atomized dispersion droplet forms an air and water vapor filled bubble on heating and collapses on drying. Displacement density is strongly affected by the amount of included air which is influenced by starch type, dispersion solids, atomization variables, and spray-dryer conditions. Packed bulk density varies with particle size distribution in the powder and smoothness of the particle surface (depth of surface depressions). The coupled jet-cooking/spray-drying process yields starch powders with higher bulk densities than conventional spray-drying when using the same high viscosity base starch.

These physical differences can be used to identify the process by which the starches were prepared when supplemented with the differences in physical structure already discussed in previous Examples. The only exception in the data is the isolated potato amylose prepared by the coupled process, which lies in region I.

Summary of Figure 7			
Process	Region	Displacement Density (g/cm^3)	Bulk Density kg/m^3 (lbs/ft^3)
Conventional jet-cooking/spray-drying	I	low	low
Coupled jet-cooking/spray-drying	II	low	high
Jet-cooking/drum-drying	III	high	low-high

Table I

Process Conditions for Jet-Cooking/Spray-Drying
High Amylose Starch (70% amylose)

	(1)	(2)	(3)	(4)	(5)
Slurry Solids	21.0	21.5	22.0	22.5	42.5
Cook Solids	13.0	13.0	13.0	13.0	28.0
Jet Cooking Temp. °C(°F)	143 (290)	143 (290)	143 (290)	143 (290)	143 (290)
Steam Flow (g./min.)	20.0	24.0	36.0	62.0	9.25 lb./min.
Cook Flow (ml./min.)	30.0	30.0	30.0	30.0	3.8 gal./min.
Nozzle Type					
Nozzle Set-up	22	22 B	22 B	22 B	1J-152
Dryer Inlet Temp. °C(°F)	220 (428)	220 (428)	220 (428)	220 (428)	230-191 (446-375)
Dryer Outlet Temp. °C(°F)	82 (180)	82 (180)	82 (180)	82 (180)	82-96 (180-205)
Atomizer Air Nm^{-2} (psig)	$1.4 \cdot 10^5$ (20.0)	$1.4 \cdot 10^5$ (20.0)	$1.4 \cdot 10^5$ (20.0)	$1.4 \cdot 10^5$ (20.0)	$8.3 \cdot 10^5$ (120.0) (steam)
Gel Strength ($g./cm.^2$)	194.0	215.0	204.0	134.0	200.1

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Table II

Process Conditions for Jet-Cooking/Spray Drying
Various High Amylose Corn Starches

	Fractionated Potato Amylose (about 100% amylose)	High Amylose Corn (about 50% Amylose)	Fluidity High Amylose Corn (about 70% amylose; about 25 $CaCl_2$ viscosity)
Slurry Solids	20.0	26.7	30.0
Cook Solids	12.5	16.0	21.0
Jet Cooking Temp. °C(°F)	154 (310)	143 (290)	143 (290)
Steam Flow (g./min.)	27.5	27.5	27.5
Cook Flow (ml./min.)	19.9	27.0	39.7
Nozzle Type	2 FLUID	2 FLUID	2 FLUID
Nozzle Set-Up	22 B	22	22
Dryer Inlet Temp. °C(°F)	225 (437)	230 (446)	220 (428)
Dryer Outlet Temp. °C(°F)	86 (187)	85 (185)	88 (190)
Atomizer Air Nm^{-2}(psig)	$2.8 \cdot 10^5$(40.0)	$1.4 \cdot 10^5$(20)	$1.4 \cdot 10^5$(20.0)
Cold Water Solubility (%)	86.6	95.3	93.0
Hot Water Solubility (%)	99.2	96.9	97.1
Gel Strength ($g./cm.^2$)	395	125	104

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Table III

Process Conditions for Jet-Cooking/Spray-Drying Other Starches

	Corn	Waxy Maize	Tapioca
Slurry Solids	20.0	20.0	20.0
Cook Solids	14.0	14.2	11.0
Jet Cook Temp. °C (°F)	143 (289)	152 (305)	160 (320)
Steam Flow (g/min)	35.0	31.0	47.0
Cook Flow (ml/min)	20.5-28.8	18.9-21.2	11.3-16.9
Nozzle Type	2 FLUID	2 FLUID	2 FLUID
Nozzle Set-Up	22B	22B	22B
Dryer Inlet Temp. °C (°F)	225 (437)	225 (437)	218 (424)
Dryer Outlet Temp. °C (°F)	86 (187)	97 (207)	95.0
(203)			
Atomizing Air Nm^{-2}(PSI)	$1.4-1.7 \cdot 10^5$ (20-25)	$1.7 \cdot 10^5$ (25.0)	$1.0 \cdot 10^5$ (15.0)
Moisture (%)	5.0	5.6	5.0
1% Solids pH	6.5	6.8	6.9
Cold Water Solubility (%)	98.6	97.7	100.0

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Claims

1. A continuous process for jet-cooking and spray-drying an inherently water-dispersible or water-soluble crystalline polymer, which comprises the steps of:

   (a) forming a slurry or a paste comprising the polymer and water;
   (b) jet-cooking the slurry or the paste with steam at a temperature of 93-177°C;
   (c) immediately conveying and introducing the jet-cooked dispersion or solution into a nozzle of a spray-dryer chamber at a temperature of 93-177°C and a pressure of $1.4\text{-}9.0 \cdot 10^5$ Nm^{-2} (20-130 psig);
   (d) atomizing the jet-cooked dispersion or solution through the nozzle with the aid of air and / or steam;
   (e) drying the atomized mist within the spray-dryer chamber at a temperature sufficient to dry the polymer; and
   (f) recovering the dried polymer as a water-dispersible or water-soluble powder.

2. A method of transforming cold-water-insoluble, partially soluble or slow to hydrate polymers into cold-water-dispersible or cold-water-soluble forms by a continuous coupled jet-cooking/spray-drying process which comprises the steps of:

   (a) forming a slurry or a paste comprising the polymer and water;
   (b) jet-cooking the slurry or the paste with steam at a temperature of 93-177°C;
   (c) immediately conveying and introducing the jet-cooked dispersion or solution into the nozzle of a spray-dryer chamber at a temperature of 93-177°C and a pressure of $1.4\text{-}9.0 \cdot 10^5$ Nm^{-2} (20-130 psig);
   (d) atomizing the jet-cooked dispersion or solution through the nozzle with the aid of air and / or steam;
   (e) drying the atomized mist within the spray-dryer chamber at a temperature sufficient to dry the polymer; and
   (f) recovering the dried polymer as a water-dispersible or water-soluble powder.

3. The process of claim 1 or 2, wherein the polymer is a fully hydrolyzed polyvinyl alcohol.

4. The process of claim 3, wherein the jet-cooking is carried out at 99-163 °C (210-325 °F).

5. The process of claim 1 or 2, wherein the polymer is locust bean gum.

6. The process of claim 1 or 2, wherein the polymer is a polygalactomannan gum and wherein the jet-cooking is carried out at 93-163 °C (200-325 °F).

7. The process of claim 1, wherein the polymer is a high amylose starch having an amylose content of 50-70 % and wherein the jet-cooking is carried out at 138-177 °C (280-350 °F); wherein the polymer is a starch having an amylose content of less than 40 % and wherein the jet-cooking is carried out at 121-162 °C (250-325 °F); or wherein the polymer is a low viscosity cold-water-soluble starch and wherein the jet-cooking is carried out at 104-148 °C (220-300 °F).

8. The process of claim 1 or 2, wherein the conveying and introducing to the nozzle is carried out at a temperature of 93-177 °C and a pressure of $1.4\text{-}9.0 \cdot 10^5$ Nm^{-2} (20-130 psig); wherein the atomizing is carried out using a pneumatic nozzle; wherein the feed pressure and gas pressure at the atomization nozzle are $1.4\text{-}10.3 \cdot 10^5$ Nm^{-2} (20-50 psig) and $1.4\text{-}12.1 \cdot 10^5$ Nm^{-2} (20-175 psig); and wherein the inlet temperature and outlet temperature in the spray-dryer are 149-246 °C (300-475 °F) and 70-107 °C (158-225 °F).

9. The process of claim 1 or 2, wherein the polymer is a mixture of a high amylose starch having an amylose content of 50 % or above and a starch having an amylose content of 40 % or less provided that the total amylose content of the mixture is 35 % or above.

10. The process of claim 1 or 2, wherein the polymer is a mixture of a starch and a polygalactomannan gum or of a starch and a fully hydrolyzed polyvinyl alcohol.

11. The process of claim 1 or 2, wherein the slurry of step (a) further comprises a water-soluble, water-dispersible, or water-insoluble compound other than the crystalline polymer; wherein the crystalline polymer is a starch; wherein the water-insoluble compound is capable of being encapsulated by the cooked starch during steps (d) to (f) or wherein the water-soluble or water-dispersible compound is capable of complexing with the starch.

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12. A pregelatinized, non-granular, modified or unmodified high amylose starch having an amylose content of above 40 %, obtainable by the process of any of the preceeding claims, further characterized in that it is substantially fully and completely disorganized as evidenced by amorphous X-ray patterns, substantially non-retrograded as evidenced by amorphous X-ray patterns and optimum gel strenghts and substantially non-degraded as evidenced by intrinsic viscosities that are similar to the base starch, and has a bulk density higher than the bulk density of the same base starch which is pregelatinized by jet-cooking and spray-drying in two separate steps.

13. The starch of claim 12, wherein the starch is modified by derivatization, conversion, and/or complexing.

14. A pregelatinized, non-granular starch powder of a starch base having an amylose content of 0 to 40 %, obtainable by the process of any of the preceeding claims, further characterized in that it is substantially non-crystalline, substantially non-degraded, and has a bulk density higher than the bulk density of the same base starch which is pregelatinized by jet-cooking and spray-drying in two separate steps.

15. A pregelatinized, spray-dried, non-granular starch powder which comprises in admixture the starch of claim 12 and claim 14.

16. The starch powder of claim 15, wherein the total amylose content of the mixture of starches is at least 35 %, characterized in that the starch powder forms a gel when dispersed in water.

Patentansprüche

1. Kontinuierliches Verfahren zum Dampfstrahlkochen und Sprühtrocknen eines an sich wasserdispergierbaren oder wasserlöslichen kristallinen Polymers, das Schritte umfaßt, bei denen:

   (a) eine das Polymer und Wasser umfassende Aufschlämmung oder Paste ausgebildet wird,
   (b) die Aufschlämmung oder die Paste mit Dampf bei einer Temperatur von 93-177°C dampfstrahlgekocht wird,
   (c) die dampfstrahlgekochte Dispersion oder Lösung bei einer Temperatur von 93-177°C und einem Druck von 1,4-9,0 x 10^5 Nm^{-2} (20-130 psig) unmittelbar weitergeleitet und in eine Düse einer Sprühtrocknerkammer eingeführt wird,
   (d) die dampfstrahlgekochte Dispersion oder Lösung mittels Luft und/oder Dampf durch die Düse zerstäubt wird,
   (e) der zerstäubte Nebel innerhalb der Sprühtrocknerkammer bei einer zum Trocknen des Polymers ausreichenden Temperatur getrocknet wird, und
   (f) das getrocknete Polymer als wasserdispergierbares oder wasserlösliches Pulver zurückgewonnen wird.

2. Verfahren zum Überführen kaltwasserunlöslicher, teilweise löslicher oder langsam hydratisierbarer Polymere in kaltwasserdispergierbare oder kaltwasserlösliche Formen durch ein kontinuierliches gekoppeltes Dampfstrahlkoch/Sprühtrocknungsverfahren, das Schritte umfaßt, bei denen:

   (a) eine das Polymer und Wasser umfassende Aufschlämmung oder Paste ausgebildet wird,
   (b) die Aufschlämmung oder die Paste mit Dampf bei einer Temperatur von 93-177°C dampfstrahlgekocht wird,
   (c) die dampfstrahlgekochte Dispersion oder Lösung bei einer Temperatur von 93-177°C und einem Druck von 1,4-9,0 x 10^5 Nm^{-2}(20-130 psig) unmittelbar weitergeleitet und in die Düse einer Sprühtrocknerkammer eingeführt wird,
   (d) die dampfstrahlgekochte Dispersion oder Lösung mittels Luft und/oder Dampf durch die Düse zerstäubt wird,
   (e) der zerstäubte Nebel in der Sprühtrocknerkammer bei einer zum Trocknen des Polymers ausreichenden Temperatur getrocknet wird, und
   (f) das getrocknete Polymer als wasserdispergierbares oder wasserlösliches Pulver zurückgewonnen wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer vollständig hydrolysierter Polyvinylalkohol ist.

4. Verfahren nach Anspruch 3, bei dem das Dampfstrahlkochen bei 99-163°C (210-325°F) durchgeführt wird.

5. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer Johannisbrotgummi ist.

6. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer ein Polygalactomannangummi ist und das Dampfstrahlkochen bei 93-163°C (200-325°F) durchgeführt wird.

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7. Verfahren nach Anspruch 1, bei dem das Polymer eine hochamylosehaltige Stärke mit einem Amylosegehalt von 50-70% ist und das Dampfstrahlkochen bei 138-177°C (280-350°F) durchgeführt wird, bei dem das Polymer eine Stärke mit einem Amylosegehalt von weniger als 40% ist und das Dampfstrahlkochen bei 121-162°C (250-325°F) durchgeführt wird oder bei dem das Polymer eine niedrigviskose kaltwasserlösliche Stärke ist und das Dampfstrahlkochen bei 104-148°C (220-300°F) durchgeführt wird.

8. Verfahren nach Anspruch 1 oder 2, bei dem das Weiterleiten und Einführen in die Düse bei einer Temperatur von 93-177°C und einem Druck von 1,4-9,0 x 10^5 Nm^{-2} (20-130 psig) durchgeführt wird, bei dem das Zerstäuben unter Verwendung einer pneumatischen Düse durchgeführt wird, bei dem der Einspeisedruck und Gasdruck an der Zerstäubungsdüse 1,4-10,3 x 10^5 Nm^{-2}(20-150 psig) und 1,4-12,1 x 10^5 Nm^{-2} (20-175 psig) sind und bei dem die Einlaßtemperatur und die Auslaßtemperatur im Sprühtrockner 149-246°C (300-475°F) und 70-107°C (158-225°F) sind.

9. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer eine Mischung einer hochamylosehaltigen Stärke mit einem Amylosegehalt von 50% oder mehr und einer Stärke mit einem Amylosegehalt von 40% oder weniger ist, mit der Maßgabe, daß der Gesamtamylosegehalt der Mischung 35% oder mehr beträgt.

10. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer eine Mischung einer Stärke und eines Polygalactomannangummis oder einer Stärke und eines vollständig hydrolysierten Polyvinylalkohols ist.

11. Verfahren nach Anspruch 1 oder 2, bei dem die Aufschlämmung in Schritt (a) außerdem eine vom kristallinen Polymer verschiedene wasserlösliche, wasserdispergierbare oder wasserunlösliche Verbindung umfaßt, bei dem das kristalline Polymer eine Stärke ist, bei dem die wasserunlösliche Verbindung während der Schritte (d)-(f) von der gekochten Stärke eingekapselt werden kann oder bei dem die wasserlösliche oder wasserdispergierbare Verbindung mit der Stärke komplexieren kann.

12. Vorgelatinierte, nichtkörnige, modifizierte oder unmodifizierte hochamylosehaltige Stärke mit einem Amylosegehalt von über 40%, erhältlich nach dem Verfahren nach einem der vorstehenden Ansprüche, ferner dadurch gekennzeichnet, daß sie im wesentlichen gänzlich und vollständig desorganisiert ist, was durch amorphe Röntgenmuster belegt wird, im wesentlichen nichtretrogradiert ist, was durch amorphe Röntgenmuster und optimale Gelfestigkeiten belegt wird, und im wesentlichen nichtabgebaut ist, was durch Grenzviskositäten belegt wird, die denjenigen der Ausgangsstärke ähnlich sind, und eine Schüttdichte aufweist, die höher ist als die Schüttdichte der gleichen Ausgangsstärke, die durch Dampfstrahlkochen und Sprühtrocknen in zwei getrennten Schritten vorgelatiniert wurde.

13. Stärke nach Anspruch 12, wobei die Stärke durch Derivatisierung, Konversion und/oder Komplexierung modifiziert ist.

14. Vorgelatiniertes, nichtkörniges Stärkepulver einer Ausgangsstärke mit einem Amylosegehalt von 0-40%, erhältlich nach dem Verfahren nach einem der vorstehenden Ansprüche, ferner dadurch gekennzeichnet, daß sie im wesentlichen nichtkristallin, im wesentlichen nichtabgebaut ist und eine Schüttdichte aufweist, die höher als die Schüttdichte der gleichen Ausgangsstärke ist, die durch Dampfstrahlkochen und Sprühtrocknen in zwei getrennten Schritten vorgelatiniert wurde.

15. Vorgelatiniertes, sprühgetrocknetes nichtkörniges Stärkepulver, das die Stärke nach Anspruch 12 und Anspruch 14 in Mischung enthält.

16. Stärkepulver nach Anspruch 15, bei dem der Gesamtamylosegehalt der Stärkemischung mindestens 35% beträgt, dadurch gekennzeichnet, daß das Stärkepulver bei Dispergierung in Wasser ein Gel bildet.

Revendications

1. Procédé continu pour la cuisson par jet de vapeur et le séchage par atomisation d'un polymère cristallin présentant de manière inhérente une dispersibilité dans l'eau ou une hydrosolubilité, qui comprend les étapes consistant :

(a) à former une suspension ou une pâte comprenant le polymère et de l'eau ;
(b) à soumettre à une cuisson par jet de vapeur la suspension ou la pâte avec de la vapeur d'eau à une température de 93 à 177°C ;

(c) à véhiculer et introduite immédiatement la dispersion ou solution, formée par cuisson par jet de vapeur, dans une buse d'une chambre d'appareil de séchage par atomisation à une température de 93 à 177°C et sous une pression de 1,4 à 9,0.10^5 Nm^{-2} (20 à 130 psig) ;
(d) à atomiser la dispersion ou solution, formée par cuisson par jet de vapeur, à travers la buse au moyen d'air et/ou de vapeur d'eau ;
(e) à sécher le brouillard d'atomisation à l'intérieur de la chambre de l'appareil de séchage par atomisation à une température suffisante pour le séchage du polymère ; et
(f) à recueillir le polymère séché, sous forme d'une poudre dispersable dans l'eau ou hydrosoluble.

2. Procédé pour transformer des polymères insolubles dans l'eau froide, partiellement solubles ou à hydratation lente en des formes dispersables dans l'eau froide ou solubles dans l'eau froide par un procédé couplé continu de cuisson par jet de vapeur/séchage par atomisation qui comprend les étapes consistant :

(a) à former une suspension ou une pâte comprenant le polymère et de l'eau ;
(b) à soumettre à une cuisson par jet de vapeur la suspension ou la pâte avec de la vapeur d'eau à une température de 93 à 177°C ;
(c) à véhiculer et introduire immédiatement la dispersion ou solution, formée par cuisson par jet de vapeur, dans la buse d'une chambre d'appareil de séchage par atomisation à une température de 93 à 177°C et sous une pression de 1,4 à 9,0.10^5 Nm^{-2} (20 à 130 psig) ;
(d) à atomiser la dispersion ou solution, formée par cuisson par jet de vapeur, à travers la buse au moyen d'air et/ou de vapeur d'eau ;
(e) à sécher le brouillard d'atomisation à l'intérieur de la chambre d'appareil de séchage par atomisation à une température suffisante pour le séchage du polymère ; et
(f) à recueillir le polymère séché, sous forme d'une poudre dispersable dans l'eau ou hydrosoluble.

3. Procédé suivant la revendication 1 ou 2, dans lequel le polymère consiste en un polymère d'alcool vinylique totalement hydrolysé.

4. Procédé suivant la revendication 3, dans lequel la cuisson par jet de vapeur est effectuée à une température de 99 à 163°C (210 à 325°F).

5. Procédé suivant la revendication 1 ou 2, dans lequel le polymère consiste en gomme de caroube.

6. Procédé suivant la revendication 1 ou 2, dans lequel le polymère est une gomme de polygalactomannane et la cuisson par jet de vapeur est effectuée à une température de 93 à 163°C (200 à 325°F).

7. Procédé suivant la revendication 1, dans lequel le polymère est un amidon à haute teneur en amylose, ayant une teneur en amylose de 50 à 70 %, et la cuisson par jet de vapeur est effectuée à une température de 138 à 177°C (280 à 350°F) ; le polymère est un amidon ayant une teneur en amylose inférieure à 40 % et la cuisson par jet de vapeur est effectuée à une température de 121 à 162°C (250 à 325°F) ; ou bien le polymère est un amidon de faible viscosité, soluble dans l'eau froide, et la cuisson par jet de vapeur est effectuée à une température de 104 à 148°C (220 à 300°F).

8. Procédé suivant la revendication 1 ou 2, dans lequel le transport à et l'introduction dans la buse sont effectués à une température de 93 à 177°C et sous une pression de 1,4 à 9,0.10^5 Nm^{-2} (20 à 130 psig) ; l'atomisation est effectuée au moyen d'une buse pneumatique ; la pression d'alimentation et la pression de gaz au niveau de la buse d'atomisation sont comprises dans l'intervalle de 1,4 à 10,3.10^5 Nm^{-2} (20 à 150 psig) et de 1,4 à 12,1.10^5 Nm^{-2} (20 à 175 psig) ; et la température d'admission et la température de sortie dans l'appareil de séchage par atomisation sont comprises dans l'intervalle de 149 à 246°C (300 à 475°F) et de 70 à 107°C (158 à 225°F).

9. Procédé suivant la revendication 1 ou 2, dans lequel le polymère consiste en un mélange d'un amidon à haute teneur en amylose, ayant une teneur en amylose égale ou supérieure à 50 % , et d'un amidon ayant une teneur en amylose égale ou inférieure à 40 %, sous réserve que la teneur totale en amylose du mélange soit égale ou supérieure à 35 %.

10. Procédé suivant la revendication 1 ou 2, dans lequel le polymère consiste en un mélange d'un amidon et d'une gomme de polygalactomannane ou d'un amidon et d'un polymère d'alcool vinylique totalement hydrolysé.

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11. Procédé suivant la revendication 1 ou 2, dans lequel la suspension de l'étape (a) comprend en outre un composé hydrosoluble, dispersable dans l'eau ou insoluble dans l'eau autre que le polymère cristallin ; le polymère cristallin est un amidon ; le composé insoluble dans l'eau est apte à l'encapsulation par l'amidon cuit au cours des étapes (d) à (f), ou bien le composé hydrosoluble ou dispersable dans l'eau est apte à la complexation avec l'amidon.

12. Amidon à haute teneur en amylose prégélatinisé, non granulaire, modifié ou non modifié, ayant une teneur en amylose supérieure à 40 %, pouvant être obtenu par le procédé suivant l'une quelconque des revendications précédentes, caractérisé en outre en ce qu'il est pratiquement totalement et complètement désorganisé comme le prouvent les diagrammes d'analyse aux rayons X correspondant à ceux d'un produit amorphe, pratiquement non rétrogradé comme le prouvent les diagrammes d'analyse aux rayons X correspondant à ceux d'un produit amorphe et les forces de gel optimales, et pratiquement non rétrogradé comme le prouvent les viscosités intrinsèques qui sont similaires à celle de l'amidon de base, et il a une densité apparente supérieure à la densité apparente du même amidon de base qui est prégélatinisé par cuisson par jet de vapeur et séchage par atomisation en deux étapes distinctes.

13. Amidon suivant la revendication 12, qui est modifié par transformation en dérivé, hydrolyse et/ou complexation.

14. Poudre d'amidon non granulaire prégélatinisée, constituée d'un amidon de base ayant une teneur en amylose de 0 à 40 %, pouvant être obtenue par le procédé suivant l'une quelconque des revendications précédentes, caractérisée en outre en ce que cet amidon est pratiquement non cristallin, pratiquement non dégradé et a une densité apparente supérieure à la densité apparente du même amidon de base qui est prégélatinisé par cuisson par jet de vapeur et séchage par atomisation en deux étapes distinctes.

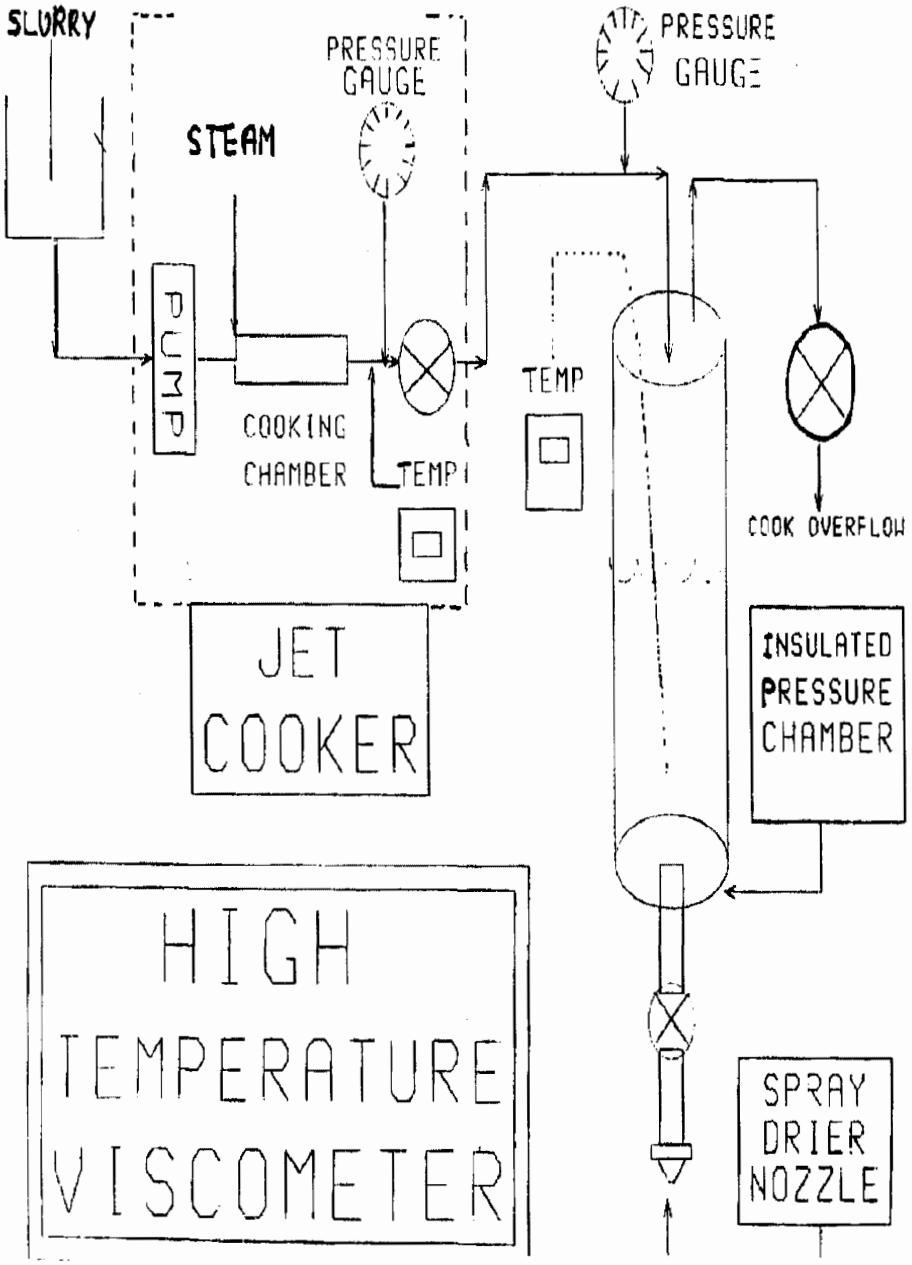
15. Poudre d'amidon non granulaire prégélatinisé, séché par atomisation, qui comprend, en mélange, l'amidon suivant la revendication 12 et l'amidon suivant la revendication 14.

16. Poudre d'amidon suivant la revendication 15, dans laquelle la teneur totale en amylose du mélange d'amidons est au moins égale à 35 %, caractérisée en ce que la poudre d'amidon forme un gel lors de la dispersion dans l'eau.

CYCLONE
COLLECTION
PROCESS
EK-22
STARCH
COOK
ATOMIZING
AIR
JET
COOKER
TEMP
CHAMBER
COOKING
PUMP
SPRAY
DRIER
HEATED
AIR
PRESSURE
GAUGE
STEAM
STARCH
SLURRY

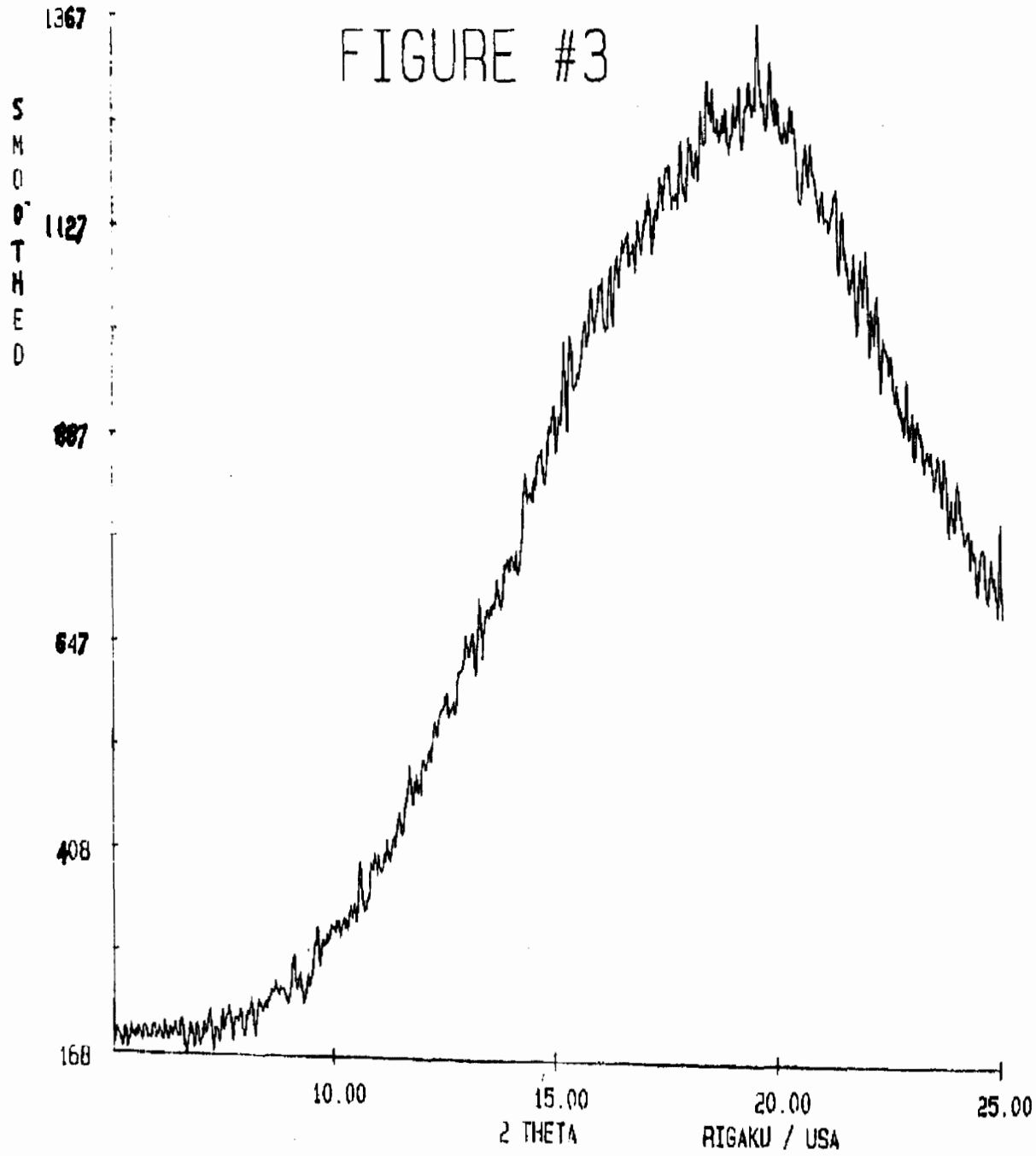
FIGURE #1

FIGURE #2



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FIGURE #3



27

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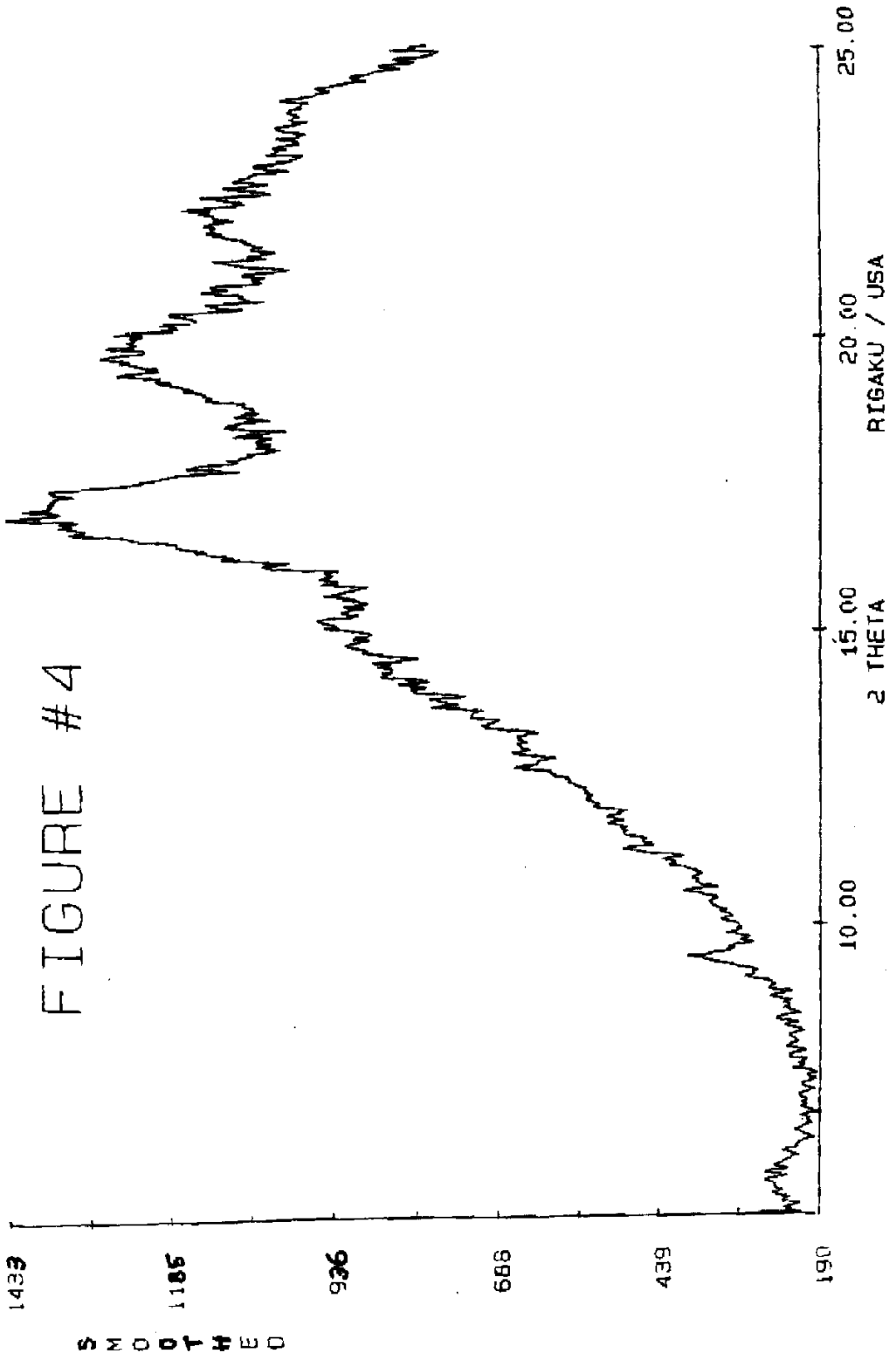

1433
1185
936
686
439
190
SMOOTHED
10.00
15.00
20.00
25.00
2 THETA
RIGAKU / USA

FIGURE #4

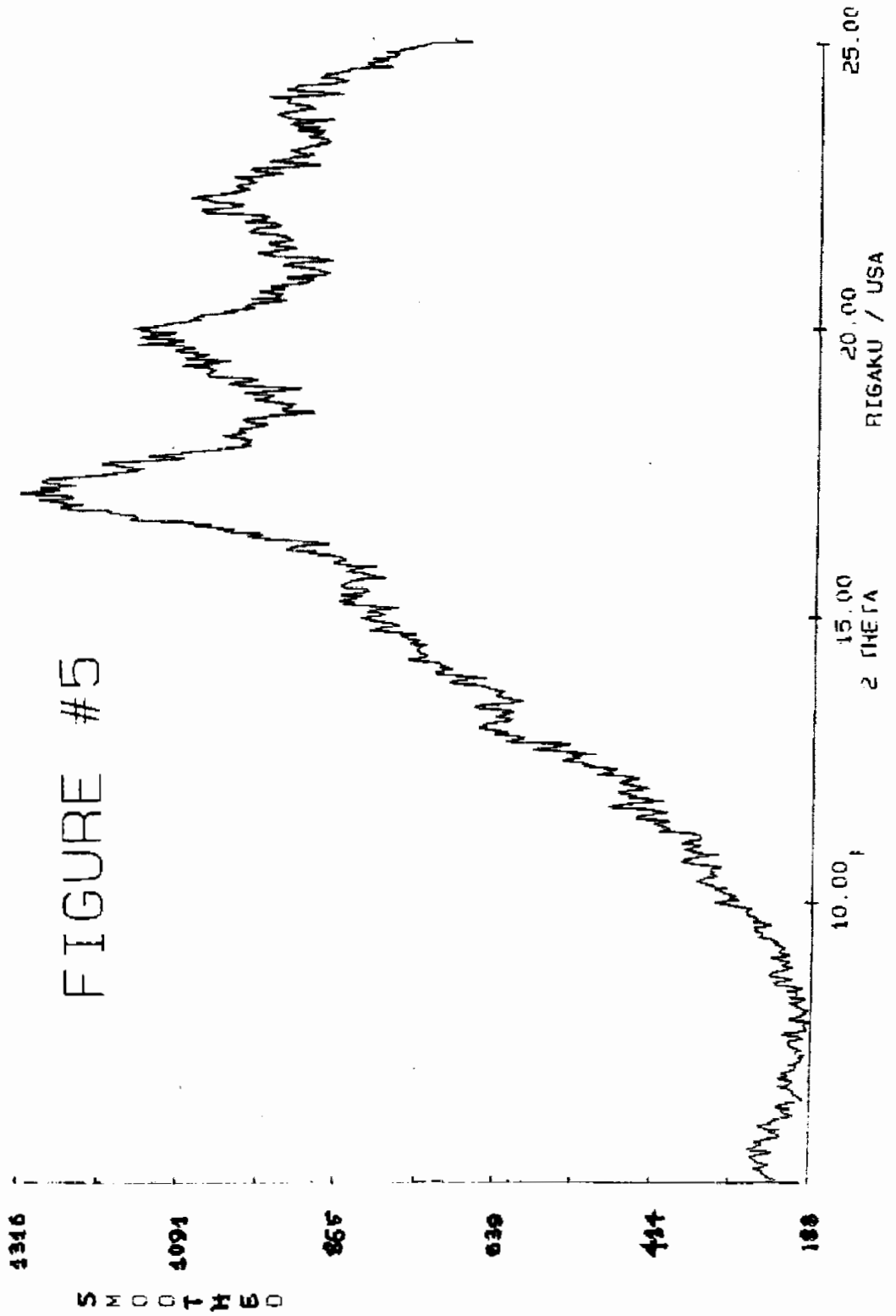
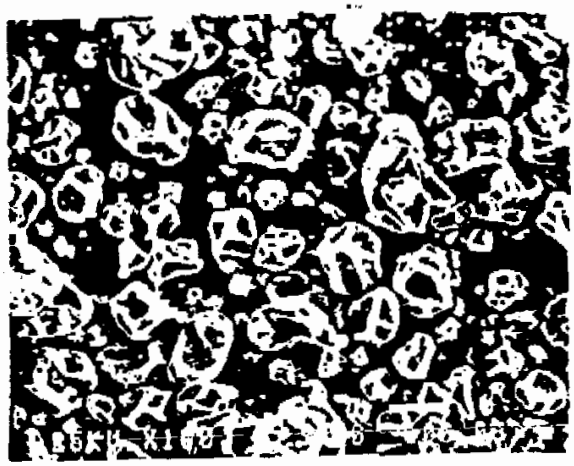

SMOOTHED
1316
1091
865
639
414
188
10.00
15.00
20.00
25.00
2 THETA
RIGAKU / USA

FIGURE #5

FIGURE #6

Pregelatinized, high amylose corn starch prepared by the coupled jet-cooking/spray-drying process.

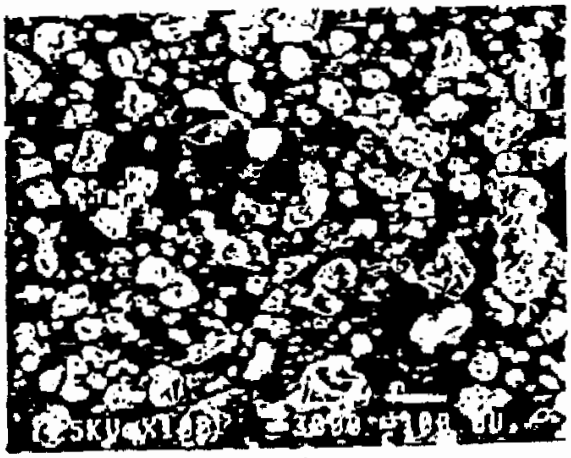
Non-granular, spray-dried particles.



PHOTOGRAPH A

Pregelatinized, high amylose corn starch prepared by the simultaneous atomization and cooking process.

Granular, spray-dried, swollen granules.



PHOTOGRAPH B

Pregelatinized, high amylose corn starch prepared by the jet-cooking/drum-drying process.

Non-granular, drum-dried particles.

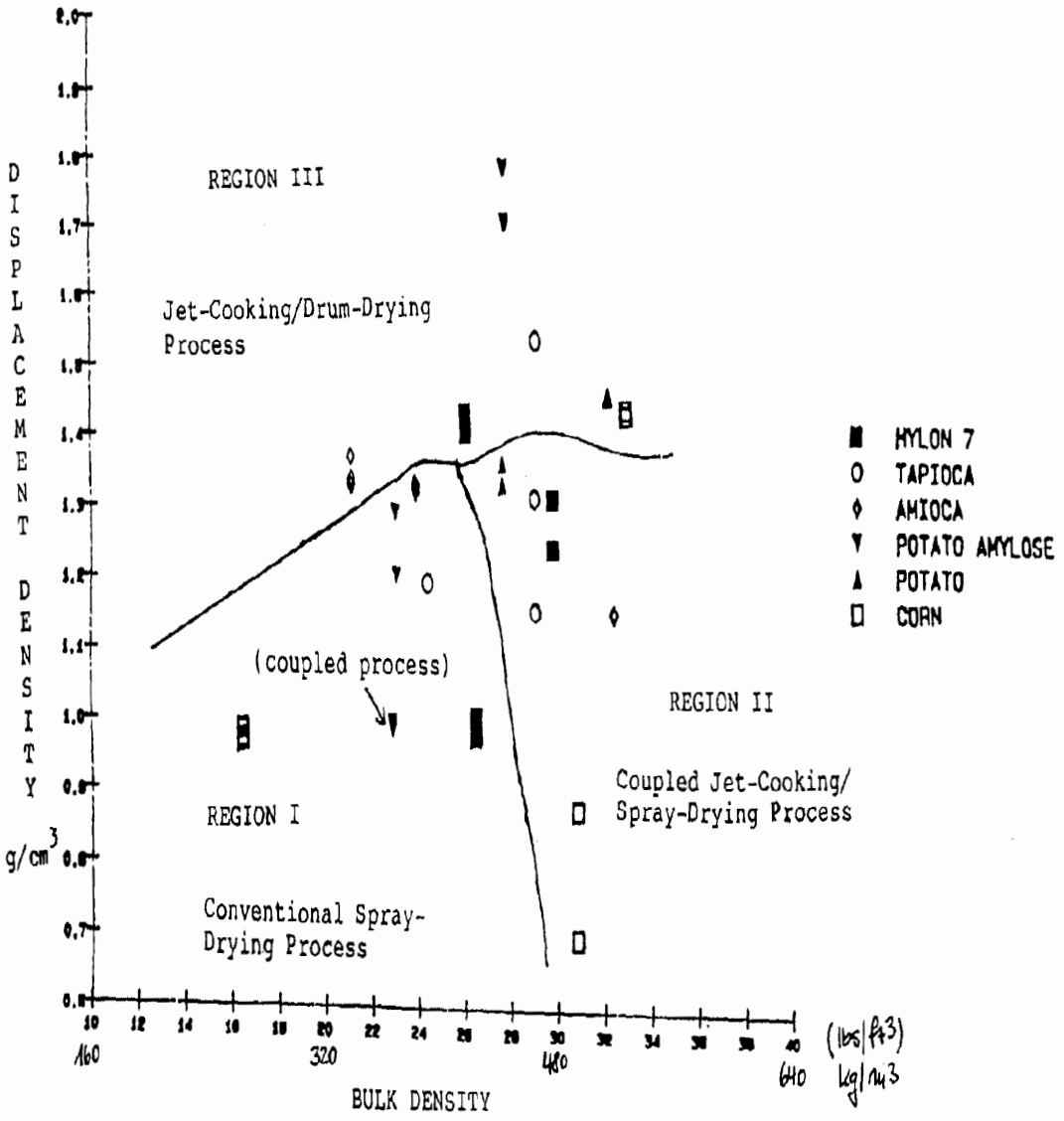


PHOTOGRAPH C

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FIGURE #7

DISPLACEMENT DENSITY VERSUS BULK DENSITY



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(54) Agglomeration process and apparatus therefor.

(57) The invention relates to a process and apparatus to agglomerate soluble coffee particles. The process comprises feeding a curtain of soluble coffee particles to an agglomerator. The curtain falls between a pair of steam distributors (66, 68) which spray steam which intersects the particles causing wetting and fusion of coffee particles to form agglomerates. The moist agglomerates pass through a tempering zone where they are partially surface dried by a draft of laminar air of a temperature less than 200°F (93.3°C) which moves downward with the agglomerates. The agglomerates are collected on a moving continuous belt (46), transferred to a drier and are subsequently dried to a moisture content of 5% or less. A process is also disclosed for darkening a light-colour, granular soluble coffee product.

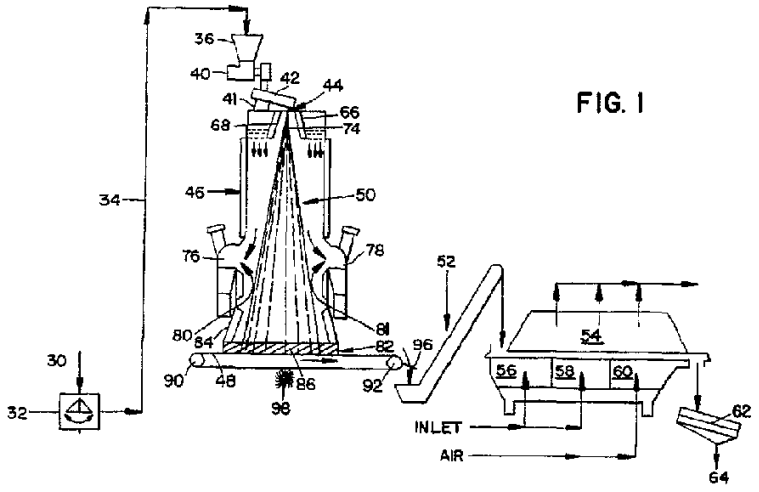


FIG. 1

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AGGLOMERATION PROCESS AND APPARATUS THEREFOR

TECHNICAL FIELD

The present invention relates to a process to effect the agglomeration of particulate comestibles, most notably soluble or instant coffee and an apparatus to effect such agglomeration.

BACKGROUND ART

Agglomeration of particulate comestibles, particularly soluble coffee powder, has been practiced in the food industry to improve the reconstitution properties of the powder (solubility), to increase the particle size to heighten consumer appeal of the product and to adjust the density of the treated product, among other reasons. Typically, when soluble coffee particles are agglomerated they are contacted with a vigorous, turbulent jet of steam. As the steam condenses, the surfaces of the particles become wet and sticky. In the turbulent steam zone these sticky particles collide and adhere to one another. Thereafter, upon drying the welds between particles solidify to produce agglomerates.

Spray drying towers have been employed to effect agglomeration. The spray-dried soluble coffee particles would be sprayed laterally into a tower where they would be contacted with a steam spray and then descend to a point of collection at the tower bottom. The agglomerates produced had a quite random particle size distribution, whereas, in addition to agglomerates, a high percent of fines were recovered, typically 35-75% of the feed material. A need still existed for an agglomerating means which would collect a narrower particle size distribution of agglomerate and/or a discharge having a lower percent of fines. To explain, a need existed for an agglomerator specifically designed and engineered for soluble coffee and like dried extracts. The agglomerator should allow independent operations in the humidification/steaming and drying to produce darker, harder agglomerated products while minimizing recycle and thereby improving volatiles retention.

U.S. Patent No. 2,977,203, issued to B. Sienkiewicz et al., teaches the traditional agglomeration of soluble coffee particles previously described. More recently, workers have attempted to modify the agglomeration process to produce agglomerates possessing a roasted and ground appearance. U.S. Patent Nos. 4,594,256, 4,594,257 and 4,594,258 have set forth a number of different processes to achieve this end. Hsu, in U.S. Patents No. 4,640,839, and 4,724,620 disclose a process and apparatus to agglomerate soluble coffee wherein coffee particles in a vertical path contact an aqueous gas which travels horizontally inward. The gas confines the soluble coffee particles under relatively quiescent conditions to moisten and fuse the particles together. Thereafter, the moistened and fused particles are dried. This process is said to be able to produce agglomerates possessing a roast and ground appearance as well as being able to darken light-colored freeze-dried coffee.

DISCLOSURE OF THE INVENTION

A process has now been developed which is ideally suited to the agglomeration of discrete particles of subdivided soluble coffee powder and other powders of use. The soluble coffee particles are discharged to the top of an elongated chamber, wherefrom a curtain of the dry particles is contacted by steam from a pair of steam distributors which are spaced from one another to produce a fine spray of steam which intersects the particles. Thereafter, the particles under a draft of laminar air are passed downwardly to partially dry the surface of the agglomerates and, finally, the agglomerates fall on a belt and proceed to a drier to produce a final agglomerate of 5% or less moisture.

The agglomeration begins as a straight curtain of powder enters the agglomeration chamber between two diverging steam distributors whose spray of steam converge on the falling curtain. A slight negative pressure in the order of less than 0.040 inches (in.) of water (10 Pa), and ideally in the order of less than 0.015 inches of water (3.7 Pa), is created at the point of entry of the curtain of subdivided particles to the agglomerator to contain the steam within the agglomeration chamber. Thus, a slight negative pressure is created relative to the atmosphere around the point of descent of the particles to the agglomerating zone. After the agglomerates leave the agglomeration zone, the moistened agglomerates spread unconfined to a reduced population density having a minimized inter-agglomerate collision. The curtain of falling agglomerates then pass freely to a tempering zone wherein at least the surfaces of the agglomerates are partially dried by a co-current, downward draft of laminar drying air, preferably at a temperature less than 200°F (93.3°C). During agglomeration the powder has undergone a moisture increase of at least 50% to as high 400% from the initial particle moisture, the wet agglomerates are at about 6-8% moisture.

The moist agglomerates free-fall and are col-

lected on a straight surface of a conveyor. Generally, the agglomerates particles collect commonly in a bed, one or two agglomerates thick, and even thicker when a coarse agglomerate is desired this being controllable by varying the belt conveyor speed. The agglomerates are eventually dried to a moisture content of 5% or less, typically such drying reduces the moisture content at least 50% and, more commonly, to a final moisture content of 3.0 to 4.5%.

The present invention also discloses an apparatus for agglomerating soluble coffee particles which comprises means for feeding a thin curtain of soluble coffee powder downwardly as a free-falling, thin curtain. Means are provided for agglomerating the thin curtain which comprises a pair of steam distributors, each having a plurality of distinct steam holes therein acting in a downward and inward opposing direction, one plate to another. A tempering zone is located beneath the agglomerating zone and is adapted to cause air to flow laminarly downward around the moistened agglomerates. A horizontal conveyor is located at the bottom of the tempering zone and is adapted to collect the moist agglomerates and transfer them to a separate drying zone wherein they may be dried in a fluidized bed or other dryer to a stable moisture content.

The foregoing apparatus is provided with means located at the upper extremity of the agglomerator that creates a slight negative pressure, say below 0.04 inches of water(10 pa)relative to the point of descent of the powder into the agglomerating zone.

The discrete steam holes are disposed as patterns thereof. These holes are adapted to spray steam inwardly at acute angles to the horizontal, the steam holes being commonly less than 1/8 of an inch (3.2 mm) and preferably less than 1/16 of an inch (1.6 mm) and being in aligned and spaced rows. Means are provided whereby the downwardly flowing laminar air cooperates with intermediate lower temperature air that contacts the downwardly circulating air whereby the product may descend gradually and be surface-dried. The agglomerates are collected on a horizontal conveyor and are transferred to a separate drying zone.

The invention has wide application and may be employed for producing dried agglomerates of spray-dried and freeze-dried coffee powder and other comestibles, such as dry dairy products like mild and cream, and dried citrus fruit juice such as orange and like juices, may be advantageously agglomerated.

The invention will thus be seen to comprise the wetting and fusion of coffee powder in a turbulent steaming zone, tempering the wetted agglomerates with warm laminer air flow, whereafter the eventual drying of the agglomerates takes place in a separate step of the process. Separate steaming and drying sections permit optimization of both independent phases of agglomeration which is not practiced in conventional agglomeration operations. The laminar flow of air in the tempering zone will generally be at a temperature less than 200°F (93.3°C) and commonly in excess of 125°F (51.7°C), more commonly 140-175°F (60-79.4°C). This exposure to heat is much less severe than in many prior art processes, thereby causing less flavor and aroma loss.

The plurality of discrete steam openings in the steam distributors have openings at 1/8" (3.2 mm) or less, ideally 1/16" (1.6 mm) or less. Two opposed steam distributors are at an angle of up to 30° from the vertical, and typically in the order of 15° from the vertical for each steam distributor.

The steam distributors are designed to provide flexibility in the zones for expansion of the steam around the location, amount and residence time in the steam zone. In some cases, the steam enters the agglomerating zone immediately at the top of the steam distributors in a manner which primarily surface wets the agglomerate, without penetration of moisture into the core. On the other hand, modifications may be practiced wherein the openings in steam distributors are located at a lower section from the point of entry of the particles into the steaming section of the design so as to cause wetting of the interior of the agglomerate to varying extents and produce a random agglomerate form.

In one embodiment, the process will produce an agglomerated instant-coffee product having a roasted and ground appearance and wherein a minimum of fines constituting generally much less than 50%, preferably from 20% to 40%, by weight of the agglomerated instant coffee is produced. Thus, as in the case of the aforesaid Zemelman, et. al., LeBlanc, et. al. and Vitti, et. al. patents, U.S. Patent Nos. 4,594,256, 4,594,257 and 4,594,258, an agglomerated instant coffee product is produced by employing the steps of milling the spray-dried coffee to produce a milled powder of an average particle size of 25 to 75 microns, optionally adding an oil, such as expressed coffee oil, to the powder or adding roast and ground colloidal particles to the powder so that such additive will bind together with slight compaction, forming a regularly shaped, loosely bound, structurally intact cluster from the powder, and fusing at least the outer surface of the cluster and leaving the interior filled with dry powder. The present invention represents the advance in the art of effecting such fusion and agglomeration and subsequently drying the agglomerates.

BRIEF DESCRIPTION OF THE DRAWINGS

Detailed description of the process will render it more apparent in terms of the coffee embodiments discussed hereinafter in connection with the accompanying figures, wherein

Figure 1 is a side elevation of the agglomerating apparatus and of the drying system;

Figure 2 is a top view of the agglomerator showing the plenum air inlets and agglomerator inlet port of the apparatus of Figure 1;

Figure 3 is a front elevation of one of the plenum air inlets;

Figure 4 is a front cross-section of the top portion of the agglomerator showing in greater detail plenum air distributors with the steam distributors removed;

Figure 5 is a side elevation of one of the pair of steam distributors of use in the present invention; and

Figure 6 is a view of the steam manifold of the distributor with parts broken away to show the manifold configuration.

BEST MODE FOR CARRYING OUT THE INVENTION

Referring to the figures, spray-dried coffee, typically particles of a spray-dried extract are advanced at 30 to a Fitzmill grinder 32 equipped with knife or hammer blade means which serve to break-up the spray-dried material into fractured particles. The subdivided soluble coffee particles are fed through line 34 to a hopper 36.

A hopper 38 is mounted above a rotary feeder 40. From feeder 40 the material enters chute 42 whereon it is deposited and wherefrom it passes into the agglomeration zone 74 through agglomerator inlet port 44. Optionally a feed funnel (not shown) can be inserted between the chute and the agglomeration zone in order to direct the powder curtain. As will be discussed hereinafter, chute 42 may be either motionless or vibrating depending upon the shape of particle ultimately intended.

From the discharge of chute 42, the material is charged to an agglomerator, broadly identified as 46, and advances downwardly onto a long, horizontal belt conveyor 48. Depending upon the agglomerate to be formed, numerous combinations may be practiced, but generally the descending spray of fine, discrete instant-coffee particles descends downwardly and is moistened. Thereafter, the action of laminar air-flows generally at 50 surface, dry the particles and prevent further expansion of the curtain.

The moist agglomerate is collected on conveyor belt 48, material being discharged to moist agglomerate transfer means 52 that carries the moist agglomerate which is eventually dried in the fluidized bed dryer at 54. Optionally, the moist agglomerate from conveyor belt 48 may be deposited directly to fluidized bed dryer 54. In the fluidized bed dryer 54, the particle-charge is deposited in a first-drying section 56, whereon the coffee particles commence their eventual drying; drying being continued in a second section as at 58 and eventually being finish dried under the influence of fluidized cooling air at 60. The dried agglomerates are discharged from dryer 54 onto a Sweco circular screen 62 and eventually are collected as product at 64.

The subdivided spray-dried coffee powder entering the agglomerator port 44 has a moisture content typically of 2.0%, although higher moisture percentages may be practiced when adding fines and milled overs. The agglomerate formed is collected at 6-8% moisture at the point of discharge from the long belt conveyor 48. Final product is recovered eventually at a moisture content of 5% or less, and typically 3-4½%, at screener 62 and product hopper 64 to achieve dark color and a discrete agglomerate form.

A distinctive part of the present process involves the use of steam distributors generally shown as 66 and 68 located at the top of agglomerator 46 and adapted to cooperate with confining walls 70 and 72 (Figure 2) to define a steaming chamber 74. Steam distributors are detailed hereinafter but, in any event, descends approximately 16-18 inches (406-457 mm) downwardly into the agglomerator 46 and are angled as shown typically at 15° from the vertical. Vertical confining walls 70 and 72 confine the discharge of the steam distributors 66 and 68 in a steaming zone.

Around the pattern of descent of agglomerates are means which assure the charging of warm temperature air, broadly below 200° F (93.3°C) ,descends downwardly with the wet agglomerates formed in chamber 74. A field of inlet air is eventually collected and ducted downwardly and outwardly as at 76, 78, exhausts being located approximately 1/3 of the agglomerator height from the base thereof. Air break means 80 and 81 generally are located beneath the exhaust, approximately 1/6 above the bottom of the agglomerator and surround the agglomerator, the air break being caused to circulate air up to and through the exhaust means 76, 78. Excess steam that may be present at the terminal section of the agglomerator is circulated upwardly by the air admitted through air breaks 80, 81 and outwardly whereby the lowermost zone of the agglomerator generally designated as 82 has virtually no steam vapor and is provided with moistened agglomerates adapted to descend and eventually deposit upon long horizontal belt conveyor 48.

To prevent moist agglomerates from contacting

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the agglomerator sidewalls, it is desired that the lower extremity of the agglomerator is tapered outwardly as shown at 84, typically also at 15° (the sides parallel to the steam distributors), from the vertical. Tapered section 84 eventually communicates with a flexible skirt, shown at 86, that maintains the agglomerate charge free of air-influx to belt 48, while at the same time allowing the charge to be advanced. Thus, tapered section 84 has an outward and downward location relative to the agglomerates descending. This allows further expansion of the agglomerate charge without contact of the agglomerator walls. Plates 66 and 68 are essentially parallel to wall members 84 in assuring descent of the particles with minimal or no contact of the agglomerator wall per se.

As a rule, the agglomerate charge on the belt means 48 is deposited thereon at a depth no greater than a half of an inch (12.7 mm), ideally as a single layer, although it is to be recognized that in less preferred embodiments a deeper layer may be employed to like advantage. The agglomerates discharged to the conveyor belt 48 retain their identity as such when run as a single layer. Thus, as the moist agglomerates proceed in a single layer along conveyor belt 48 at the aforestated moisture content of 6-8%, the vast majority thereof are in limited contact with one another. In the less preferred embodiment where a coarser agglomerate is desired, the belt speed is decreased to obtain multiple layers of agglomerates which will fuse together to form larger aggregates.

The conveyor belt 48 comprises rollers 90, 92 and the belt itself 48 of white neoprene rubber. A blade 96 scrapes the belt clean of agglomerates and is further equipped with a rotating brush 98 that scrapes the belt clean of any coffee fines, whereupon the belt continues endlessly once again to receive successive agglomerate charges.

It should be noted at this point that there is a minimal entry of surrounding atmospheric air entering into the lowermost zone 82 of the agglomerating chamber beneath the flexible skirt 86. This air helps to remove excess steam and/or moisture in this area.

As indicated previously, tempering occurs at a relatively low temperature and ideally above 140° F (60° C) inlet air, although typically as high as 175° F (79.4° C) and higher can be employed. This warm air is blown into the top of the agglomerator through four air distributors 100, 102, 104 and 106 (shown in Figure 2). Air enters each distributor at 108 and courses through the air distributors where it is subdivided respectively into channels of expanding dimension 112, 114, 116, 118 (shown in Figure 3) that thereafter feed the charge of warm air downwardly as at 120 found the steaming chamber 74 of agglomerator 46. The four air distributors thus shown enter the agglomerator 46 and 68 that surrounds steaming zone 74 wherein steam distributor 66 and the end walls 70, 72 are located.

In the present process, agglomeration is affected in a relatively turbulent manner by passing discrete particles of subdivided dry feed having a moisture content less than 3%. The convergent steam sprays emanating from 66, 68 intersect with a thin stream of discrete particles that descent into the agglomerator.

The steam sprays are established by a plurality of discrete holes in the steam distributors adapted to issue the steam therethrough; each of the steam sprays intersect the curtain of powder as it descends in agglomeration zone 74. The steam is generated uniformly and to an extent which at least doubles the moisture content of the product passing the steam sprays causing the agglomeration.

The steaming zones are formed by rows of downwardly and inwardly poised, discrete sprays of steam which intersect with the downward plane of the curtain of product, each steam spray being poised to intersect the downward descent of particles as they are wetted to form agglomerate clusters. The tiny holes, are generally less than 1/8" of an inch (3.2 mm) and typically 1/16 of an inch (1.6 mm), the holes being arranged in order uniformly along the length of each plate. Each of the plates of surfaces 68, 68 are poised at the same angle to the vertical, whereby the agglomerates formed are uniformly wetted with steam.

Referring to Figs. 5 and 6, a steam distributor 66 is shown. In Fig. 5 perforated face plate 100 and mesh screen 138 are shown with holding screw 102 on the face plate 100 and holding screens 142 on mesh screen 138. In Fig. 6 the mesh screen 138 and the perforated face plate 100 are not shown. Steam distributor 66 is shown with a steam manifold 134 having six pipe legs 122, 124, 126, 128, 130 and 132. Entrance steam pipe 136 is shown feeding manifold 134. The steam holes exiting the six pipes 122, 124, 126, 128, 130 and 132 are not shown (as they face the back of the distributor housing) but approximately 9 holes per pipe leg, having an opening of 3/32 inch (2.4 mm), are used to provide uniform velocity across the distributor. Condensate drain line 140 is also shown. The above structive for steam distributor 66 is repeated for a similar distributor 68.

It is a feature of the present process that a plurality of the aforementioned small holes, which holes may be in the neighborhood of 1,000 or more, depending upon lateral size of the agglomerator may be employed; the holes being variously located for various product curtain characteristics. In one embodiment, strips of small holes may be located immediately adjacent to the entry to the upper portion of the agglomerating zone 74.

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In such an embodiment for the production of soluble coffee having a roast and ground appearance, the surface of the agglomerate principally is wetted, leaving the interior relatively dry.

In other embodiments, the small holes arranged in lines that are preferably alternating are located in the lower 50% of the respective faces of perforated plates 66, 68; such an embodiment will cause individual particles of powder to become more wetted and fused together to form larger, random agglomerates.

Indeed, the process also contemplates strips of tiny holes in the central 1/3 of the perforated plates. This allows the coffee particles to descend prior to contact with the steam. This contact will result in less initial steam contact to darken an already-formed agglomerate or darken a freeze-dried product as desired.

The wet agglomerates continue downwardly between distributors 66 and 68 and come into contact with warm, temperature drying air moving laminarly downward in the agglomerator 46, the drying air temperature being introduced to the agglomerator at a temperature commonly less than 200°F (93.3°C) but greater than 125°F (51.7°C), commonly 140 to 175°F (60 to 79.4°C). The warm temperature air will pass downwardly through the agglomerator a substantial distance, whereupon it intermixes with an updraft of a still lower at room temperature air from the air break 80 and 81, commonly air at room temperature of abcut 68°F (20°C). Thus, at the lower extremity of the tempering zone, the warm air, mixed with the updrafted air, moves outwardly away from the descending agglomerates which collect as a bed thereof downstream of the air exhaust as a curtain of discrete particles.

Means are provided for drying the moist agglomerates thus collected to remove at least 50% of the moisture thereof, preferably in fluidized bed dryer 54, and collect same at a moisture content less than 5%, commonly in the case of soluble coffee at 3-4.5%.

The agglomerator wall is intended to serve the distinct function of essentially containing laminar flow therewithin from the plenum section at the upper extremity of the agglomerator and continuing downwardly to the exhaust ducts 76, 78. The flow that occurs in the tempering zone of the device is entirely laminar flow, i.e., having a Reynolds Number value much less than 2300. It may be granted that the chamber volume intermediate steam distributors 66, 68 and in the vicinity of 74 is turbulent by reason of the downward spray of inlet powder and the angle at which the steam is introduced. However, as the particles intermingle with the steam spray they descend downwardly and outwardly as shown, whereupon they are contacted by the downwardly laminarily flowing air which contacts and surface dries the particles in the tempering zone.

Thus, in an agglomerator unit of a size about 5ft.(1.52 square, the plenum directs the warm air downwardly around the rectangular outline of the agglomeration zone 74 wherein the steam and particles collide to effect initial agglomeration. The inlet plenum air which courses downwardly at typically 1000c.f.m. (471947 cm^3/sec) and as high as 2000 c.f.m. (943895 cm^3/sec), intercepts the agglomerates formed; the feed rate of the coffee powder being 300 pounds per hour (3266 kg/day).

Within the laminar flow pattern that exists, the tempering continues as the particles continue their downward and gradual outward descent until they typically have been at least surface dried.

The inlet port created by the distributors 66, 68 is maintained at a slight negative pressure of 0.010 to 0.040 in. of water (2.49 to 10 Pa). Such negative pressure keeps the agglomerating steam in the chamber 74. The slight negative pressure is maintained by controlling the plenum air. A balance is maintained between the inlet plenum air and the exhaust of air, a variable speed fan (not shown) being employed to regulate the plenum flow. The fan means comprise an exhaust fan communicating through exhaust ducts to cyclones which are in line to collect dust particles escaping the agglomerator. The ducts merge and then communicate with exhaust fan. By adjusting the speed of the plenum fan, the slight negative pressure, aforesaid, is maintained to assure that the agglomerates fall in a more consistent pattern.

With continued downward flow of moist agglomerates, the agglomerates thereof usually experience a slight dehydration, commonly less than 0.5%, generally referred to as surface-drying. The continued fall of the agglomerates eventually collect on belt 48. The outward slant of skirt 84 assures an uninterrupted migration of agglomerate particles downwardly for deposit on belt 48.

Referring to distributors 66, 68, the steam will generally issue as two rolling intersecting patterns. This turbulence all occurs substantially within the chamber 74, whereafter the wetted agglomerates proceed downwardly and outwardly under the control of the drying actions of the laminarly descending air.

When a random, honeycomb agglomerate is desired, face plates 66, 68 having the discrete perforated holes on the lower sections thereof are used. Some flaring of the powder charge prior to primary steam contact at about 6 p.s.i. (142kPa is desired which produces a more random agglomerate form. The flow pattern of the particles is such that the steam flow allows the particles to widen somewhat as they descend. The majority of the

steam jets are generally in the lower half of the face of each distributor, it being understood that some minority of the jets may be located above the midpoint. Such a product is achieved commonly without agitation of the coffee powder entering the agglomerator, i.e., the vibrator 42 is not employed. A spray-dried feed, before milling customarily within the 75-120 microns average particle size, will be ground to a particle size of from 20-70 microns with a standard deviation of 35-75%.According to the present invention, it is also possible to produce an agglomerated instant coffee product possessing an appearance much like roasted and ground coffee. A very cohesive powder is sought and oil may be plated on the surface of the spray-dried powder prior to milling. Alternately, colloidal roast and ground coffee may be mixed with the soluble coffee to increase the cohesive nature of the powder. The milled powder will be vibrated to effect a displacement of say about0.2" (5.1 mm) at 60 cycles per second of vibration. The coffee charge to tray 42 will cluster, due to vibration of the vibrator 41, thereafter feeding a vibrating screen and the discharge having a distinct shape, i. e., a charge passing through to a 6 to 8 mesh U.S. Standard Sieve screen (3.35 to 2.36 mm). The resulting dried agglomerate particles have distinct cube-type shapes.

To assure the clusters remain intact, they are contacted by steam at 6 p.s.i. (41.37 kPa) through face plate holes near the top half of each distributor, resulting in intersecting steam sprays that directly contact the descending clusters and produce wetted exteriors on the faces thereof. The agglomerated cluster will be a size ranging from a 6 mesh to say 10 mesh (3.35 to 2.00 mm), 8 mesh (2.36 mm) being preferred, and will have a fines percent less than 35% and commonly less than 25%, say 20%. The agglomerated particle dries as a dark cluster, having a roasted and ground appearance whose center contains unagglomerated powder. The agglomerated product exhibits substantially higher volatile retention and improved product quality due to significantly lower recycle rates.

The apparatus and process of the present invention may also be utilized to agglomerate a mixture of two distinct soluble coffee products, such as coagglomerating a mixture of soluble coffee flakes and spray-dried soluble coffee powder (either milled or unmilled). In similar fashion, the apparatus and process may be utilized to darken a light-colored, granular, soluble coffee product (such as freeze-dried soluble coffee) with a minimal steam to coffee ratio, typically less than 0.1, preferably from 0.03 to 0.09 lbs. of steam to lbs. of coffee-(0.03 to 0.09 kg of steam to 1 kg of coffee). When darkening granular soluble coffee products it is possible to achieve up to a 10 Lumetron colour unit darkening (i.e. from a light-colored freeze-dried coffee of 34° L units to a finished, darkened product of 24° L units). The darkening can be achieved with a minimal density increase within the range of from 10 to 25% depending upon the degree of darkening. The minimal increase in density results from the fact that there is only minimal steam penetration into the coffee product. In addition to the darkening and density increase, the process will improve the hardness value of the soluble coffee and it has the capability to remove substantially all of the fines.

EXAMPLES

Example #1

This example shall describe the production of a dark coffee agglomerate.

A spray-dried soluble coffee powder, having a bulk density of about 0.26 g/cc and a moisture of between 2.0-3.0% produced via conventional high viscosity spray drying is milled in a Fitzmill Model D grinder to an average particle size of 50 microns. The resulting milled powder has a density of between 0.5-0.6 g/cc. Milling may also be performed on a Micropul mill with a classifier. If desired, recycle can be mixed with the fresh coffee powder in a ribbon mixer before grinding.

The milled coffee powder is fed to the hopper of a rotary feed. The rotary feed is operated at a rate, typically 20-30 rpm, that yields a powder feed rate of 250-300 lbs/hr (113.4-136.1 kg/hr) to the motionless feed chute. Angled at 20 to 40 degrees from the horizontal, the feed chute allows the coffee powder to descend in a uniform curtain to the feed funnel. The funnel accepts the powder through a motionless 6-mesh (3.35 mm) screen and directs it through the 2½ inch x 12 inch (63.5 mm x 304.8 mm) agglomerator feed port and into the steaming zone. Steam enters the zone via two 2 ft. x 1.5 ft. (609.6 mm x 457.2 mm) steam distributors running parallel to the port and angled 15° from vertical. Perforated plate faceplates direct the steam into the steaming zone (agglomeration zone). Wet steam at 4-8 psig (129-159 kPa) is supplied to the distributors at a flow rate of less than 700 lb/hr (317.5 kg/hr).

The random coffee agglomerates formed from the steaming zone fall through the agglomerator to the tempering zone. Warm air of 140-150° F (60-65.6° C) is blown into the plenum air chamber surrounding the steaming zone at a flow rate of about 1900 ACFM (54 m ^{3}/min measured at 1 bar) in order to maintain a 0.01-.015 in. H_2O, (2.5-3.7

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Pa) negative pressure at the feed port. About 47 ACFM (1.33 m^3/min measured at 1 bar) of ambient air is drawn into the feed port, thus keeping the steam in the steaming zone. Air is exhausted from the 5 ft. x 1.5 ft. (1524 mm x 457 mm) high exhaust, located 4 ft. (1219 mm) from the agglomerator base, running parallel to the feed port at a constant rate of 3200 ACFM (91 m^3/min measured at 1 bar). The exhaust airflows are balanced by bleeding ambient supplemental air into the exhaust hoods. The total volume of supplemental air is 980 ACFM (27.8 m^3/min measured at 1 bar). Ambient air is drawn into the air break at a rate of 370 ACFM (10.5 m^3/min measured at 1 bar). The balance of the inlet plenum air, supplemental air, and exhaust streams are sensed by Dwyer 20 model #2304 magnehelic gauges. Condensation of steam on the agglomerator walls is prevented by recirculating 300 CFM (8.53 m^3/min measured at 1 bar of 180° F (82.2° C) air through the 3 inch (76 mm) deep agglomerator shell.

The moist agglomerate, about 6.1% H_2O falls upon the custom-made, 6ft. x 15 ft. long (1828 mm x 4572 mm long) white, neoprene belt conveyor and is conveyed from the agglomerator at a rate of between 120 to 160 ft/min (610 to 813 mm/sec). The thickness of the coffee layer on the belt is kept as low as possible to avoid clumping of agglomerates. At the end of the conveyor, the agglomerate falls through a stainless steel transition into a collection bin which is used to transfer moist agglomerates to the dryer feed hopper. A motorized brush beneath the belt is run at full speed to keep the belt free of coffee build-up.

Moist agglomerates are fed to the product dryer via an Eriez HS-50 vibratory feeder. The dryer used is a Jeffry TMV 2 ft. wide x 15 ft. long (610 mm wide x 4572 mm long), vibrating, fluid-bed dryer with three 2 ft. x 5 ft. (610 x 1824 mm) long sections and adjustable stroke lengths. A stroke length of 1/8 inch (3.2 mm) is used to yield a 2 minute residence time in the dryer. The first two sections of the dryer are each supplied with 1000 ACFM (28.4 m ^{3}/min measured at 1 bar) of 180-190° F (82.2-87.8° C) air for drying while the third section receives 1000 ACFM (28.4 m^3/min measured at 1 bar) of 55-60° F (12.8-15.6° C) air for product cooling. The dried agglomerate, about 4.5-5.% H_2O, exits the dryer and is passed through an 18 inch (457 mm) diameter Sweco screener, 16 model #LS18S3333, with the product collected being all agglomerate falling through an 8 U.S. mesh (2.36 mm) screen and resting on a 20 U.S. mesh (850 um) screen, although other screen sizes may be used. A product of about 0.23 g/cc density, 16.0° L color, and less than 10% fines results.

Example #2

This example shall describe the production of a co-agglomerate soluble coffee product, specifically an agglomerate produced from a mixture of milled spray-dried soluble coffee and soluble coffee flakes.

As in example #1 spray-dried soluble coffee powder is milled. The milled coffee powder is then mixed with coffee flakes, produced via a separate coffee process, at a ratio of 7 to 3 in a ribbon blender. The powder/flakes mixture is thus transferred to the hopper of the rotary feeder and agglomerated as in example #1. A product of about 0.23 g/cc density, 19.5° L color, 4.5% H_2O and less than 10% fines resulted. The finished product exhibits a dark crystal-like, shiny appearance.

Example #3

This example describes the production of an agglomerated coffee product having a roast and ground appearance.

A spray-dried soluble coffee powder is milled as in example #1 with the exception that a mill with a classifier is recommended. The milled powder is transferred to the hopper of the rotary feeder and fed to the agglomerator at rates of 150-200 lb/hr (68.04-90.72 kg/hr). The motionless feed chute of example #1 is replaced by a 10 inch x 26 inch long (254 mm x 660 mm long) vibrating tray, powered by an Eriez HS-40-1 drive, with diverters to distribute the power across its entire width. As the powder falls from the discharge end of the tray it falls onto the two end-driven vibrating formation screens placed above the port. The screens are contained in custom-made, "U-box" size frames and are vibrated parallel to the port opening via Eriez HS-20 drives.

The vibration of the formation screens may be controlled via rheostats to obtain bridging. Distributor steam pressures of less than 5 psig (135 kPa) are used to provide gentle steaming. The other agglomeration, drying, and handling conditions are as in example #1. A product of about 0.28 g/cc density, 20.5° L color, and less than 10% fines results.

Example #4

This example describes the use of the present apparatus to darken a freeze-dried soluble coffee product.

Freeze-dried coffee particles of about 0.21 g/cc density, 3.7% H_2O, and 33° L color are fed to the hopper of a silotta vibratory feeder. The vibratory

feeder is used to avoid damaging the particles. From the vibratory feeder the coffee is fed to the agglomerator inlet port at a rate of 800-1000 lb/hr (362.9-435.6 kg/hr). Corresponding amount of steam is approximately 40 to 45 lbs (18.1 to 20.41 kg) an hour yielding a steam to coffee ratio of approximately 0.05.

In the steaming zone the coffee particles are exposed to steam of less than 3 psig (122 kPa) pressure. A 0.015 in H_2O (3.74 Pa) negative is maintained at the feed port. The agglomerator airflows and temperatures 18 are similar to those of example #1. The darkened freeze-dried particles are dried in the Jeffrey TMV 2 ft. x 15 ft. (610 mm x 4572 mm) long vibrating, fluid-bed dryer example #1 with slightly lower temperatures being used as in (170°F [76.7°C], 170°F [76.7°C], 50°F [10°C]). The resulting product is darkened to 25.5-26.5°L color, with a density and moisture of 0.26 g/cc and 3.8-3.9% respectively.

Claims

1. A process for agglomeration of soluble coffee particles which comprises:

(a) feeding a curtain of soluble coffee particles into an agglomerator between two separate steam distributors poised to intersect the particles as they descend therein;

(b) contacting the particles with a fine spray of steam which intersects the particles causing wetting and fusion of coffee particles to form agglomerates;

(c) passing the falling agglomerates to a tempering zone wherein the agglomerates are partially surface dried by a draft of laminar air which moves downward with said agglomerates, said laminar air being at a temperature of less than 200°F (93.3°C);

(d) collecting the partially surface dried agglomerates on a moving continuous belt;

(e) transferring the agglomerates to a drier; and

(f) drying the agglomerates to a moisture content of 5% or less.

2. A process for darkening a light-coloured, granular soluble coffee product which comprises:

(a) feeding a curtain of soluble coffee product into an agglomerator between two separate steam distributors poised to intersect the product as it descends therein;

b) contacting the soluble coffee product with a fine spray of steam which intersects the product causing wetting of coffee product the contact of steam to coffee being maintained at a steam to coffee ratio of less than 0.1;

c) passing the falling wetted product to a tempering zone where the wetted product is partially surfaced dried by a draft of laminar air which moves downward with said wetted product said laminar air being at a temperature of less than 200°F (93.3°C);

(d) collecting the partially surface dried product on a moving continuous belt;

(e) transferring the product to a drier;

(f) drying the product to a moisture content of 5% or less.

3. A process according to Claim 2, wherein the charge of light colored, granular soluble coffee is freeze-dried soluble coffee.

4. A process of Claim 2 or Claim 3, wherein the steam to coffee ratio varies from 0.03 to 0.9.

5. A process according to any one of Claims 1 to 4, wherein a slight negative pressure is created relative to the atmosphere thereabout at the point of descent of the particles to the agglomerator.

6. A process according to Claim 5, wherein the negative pressure is less than 0.04 inches of water (10 Pa).

7. A process according to any one of Claims 1 to 6, wherein the laminar air in the tempering zone is at temperature exceeding 125°F (51.7°C).

8. A process according to Claim 7, wherein the laminar air is between 140°-175°F (60°-79.4°C).

9. A process according to any one of Claims 1 to 8, wherein the steam distributors are planar and located at acute vertical angles to the horizontal.

10. A process according to Claim 9 wherein the planes of each of the steam distributors are at an angle of up to 30° from the vertical.

11. A process for according to Claim 9 or Claim 10, wherein the steam distributors are at an angle of about 15° from the vertical.

12. A process according to any one of Claims 1 to 11, wherein each of the steam distributors is comprised of a multiplicity of discrete tiny hole areas which spray the curtain of coffee particles.

13. A process according to Claim 12, wherein the tiny holes are arranged as a plurality of rows thereof and are adapted to direct steam inwardly and downwardly.

14. A process according to Claim 12 or Claim 13, wherein each of the small holes are less than 1/8 of an inch (3.2 mm).

15. A process according to any one of Claims 1 to 14, wherein the agglomerates are dried and cooled in a fluidized bed dryer in step (f).

16. A process according to any one of Claims 1 to 15, wherein the charge of soluble coffee particles is spray-dried powder that has been ground after spray-drying.

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17. A process according to any one of Claims 1 to 16 wherein the agglomerate possesses a roast and ground appearance which process further comprises the steps of:

(a) milling spray-dried powder to an average particle size of from 25 to 75 microns, said powder forming the curtain of soluble coffee particles in step (a);

(b) prior to steam contact vibrating the milled spray-dried powder to form clusters which are passed through a screen; and

(c) fusing the outside surface of the cluster in step (b) while leaving the interior filled with dry powder.

18. A process according to Claim 17, wherein the spray-dried powder has added thereto coffee oil.

19. A process for agglomeration according to Claim 17 or Claim 18, wherein the spray dried powder has added thereto colloidal roast and ground coffee.

20. Apparatus for agglomerating soluble coffee particles comprising:

(a) means (42) for feeding a thin curtain of soluble coffee powder downwardly as a free-falling, thin curtain;

(b) an agglomerating zone (46) comprising a pair of steam distributors (66, 68), each having a plurality of discrete steam holes therein adapted to contact the curtain with steam sprays in downward and inward opposing directions;

(c) a tempering zone adapted to cause air at a temperature below 200° F (93.3° C) to flow laminarly downward around the moistened agglomerates;

(d) a conveyor belt (48) at the bottom of the tempering zone adapted to collect the moist agglomerates; and

(e) a separate drying zone (54) for drying the moist agglomerates thus recovered to a stable moisture content.

21. Apparatus according to Claim 20, wherein means are located at the upper extremity of the agglomerating zone creating a slight negative pressure relative to the point of descent of the powder into the agglomerating zone.

22. Apparatus according to Claim 20, wherein the negative pressure is less than 0.04 inches of water (10 Pa).

23. Apparatus according to any one of Claims 20 to 22, wherein the air in the tempering zone is at a temperature greater than 125° F (51.7° C).

24. Apparatus according to any one of Claims 20 to 23, wherein the air in the tempering zone is between 140° -175° F (60° -79.4° C).

25. Apparatus according to any one of Claims 20 to 24, wherein the steam distributors (66, 68) are planar and are equally spaced from the curtain of falling coffee are equally spaced from the curtain of falling coffee particles.

26. Apparatus according to any one of Claims 20 to 25, wherein the planes of each of said steam distributors (66, 68) is at an angle of up to 30° from the vertical.

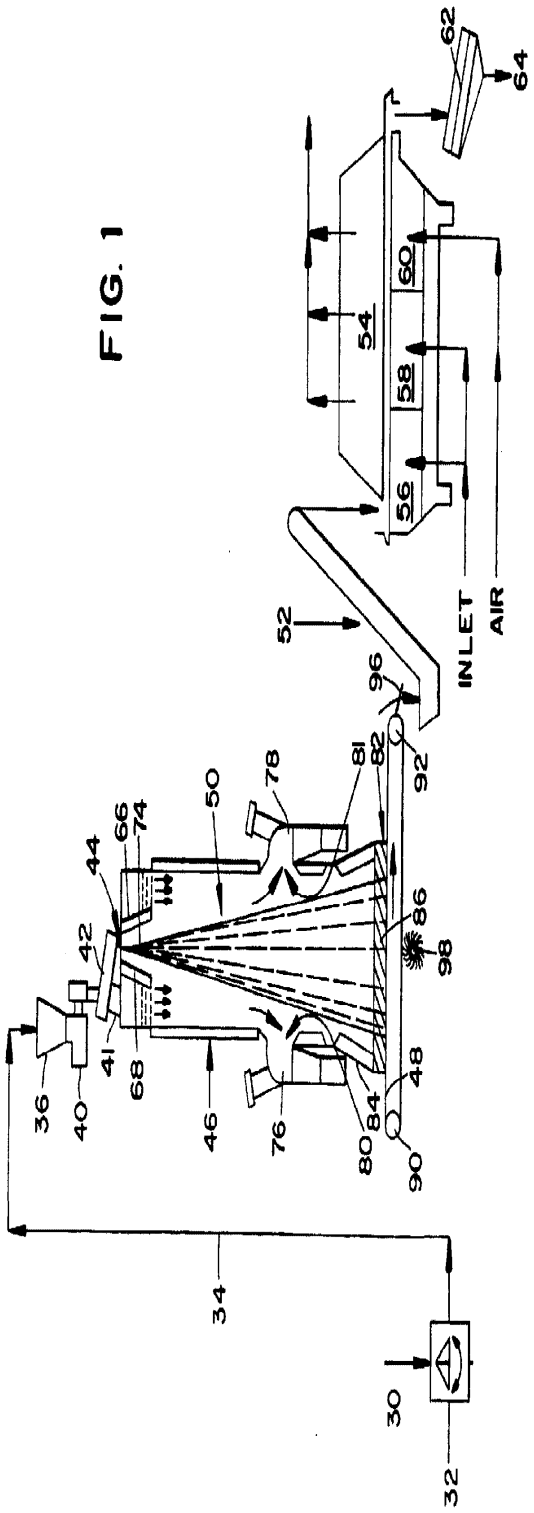
27. Apparatus according to Claim 26, wherein the steam distributors are at an angle of about 15° from the vertical.

28. Apparatus according to any one of Claims 20 to 27, wherein the holes in the steam distributor have openings less than 1/8" (3.22 mm).

29. Apparatus according to any one of Claims 20 to 28, wherein the separate drying zone (54) is a fluidized bed dryer.

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FIG. 1



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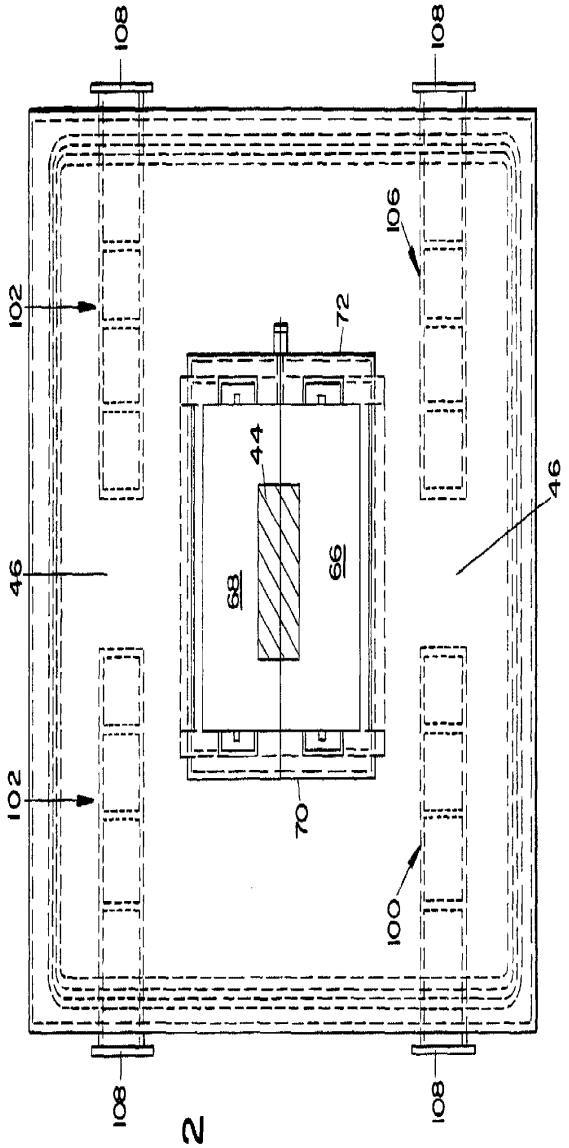


FIG. 2

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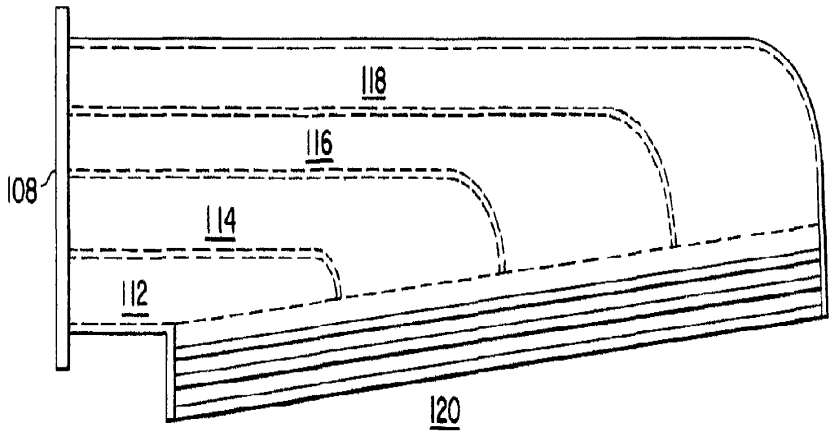
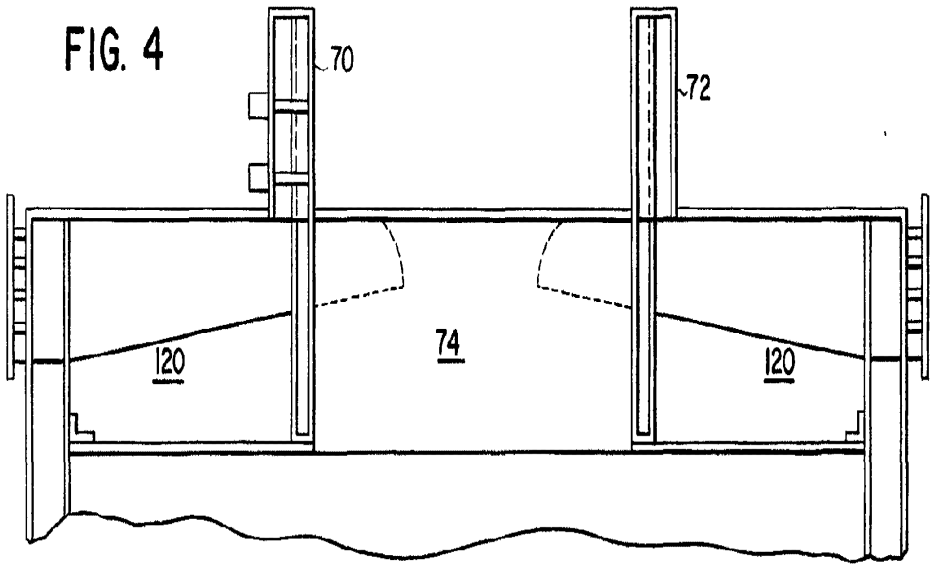


FIG. 3

FIG. 4



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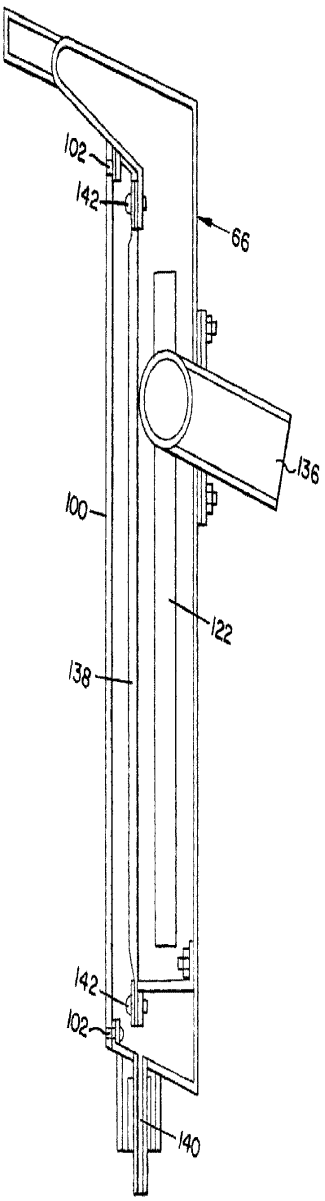
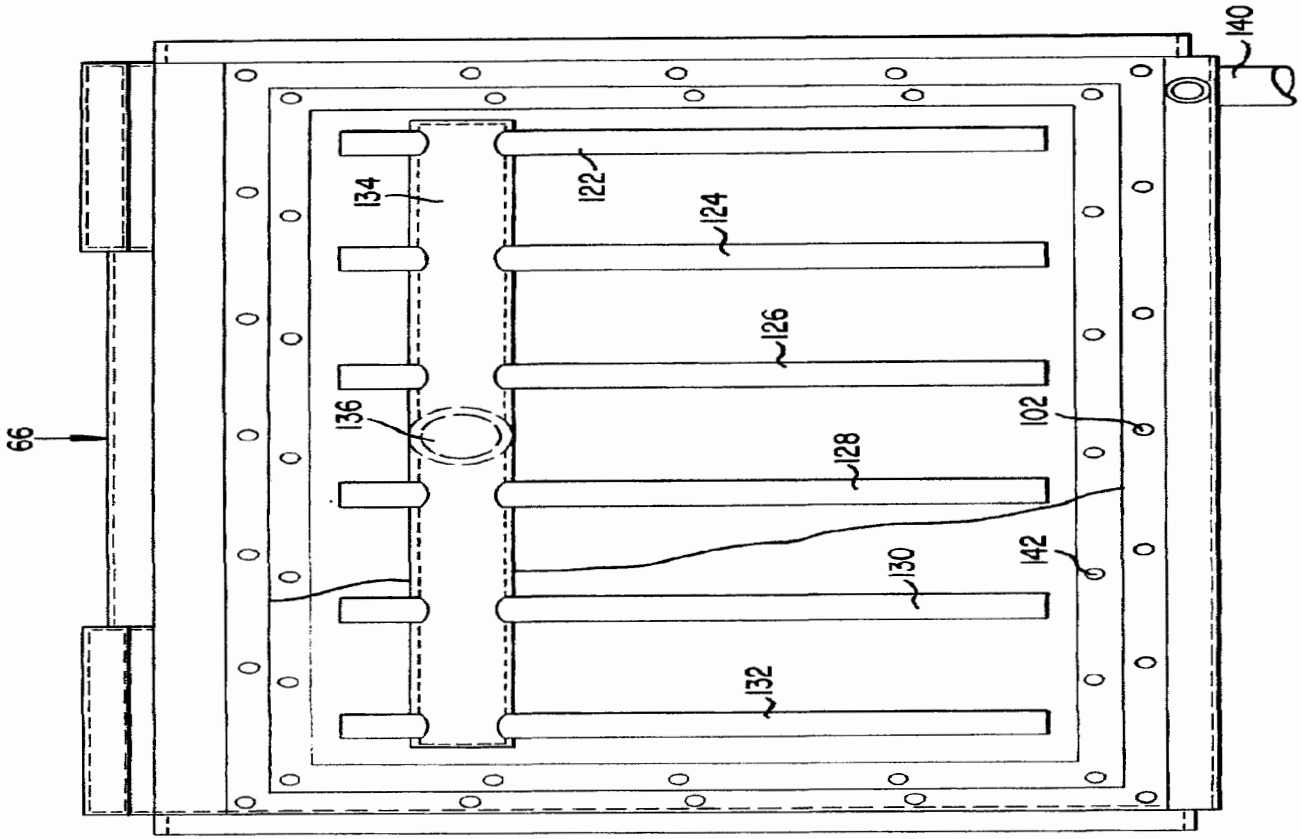


FIG. 5

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FIG. 6



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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 0320

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	FR-A-1 513 730 (GENERAL FOODS) * Example 1 *	1,2,7,8, 12,13,16, 20,23,24, 28	A 23 F 5/38 A 23 P 1/02
Y	US-A-2 893 871 (H. GRIFFIN) * Claims 1-3; columns 1-4; column 6, line 63 - column 7, line 40; column 10, line 51 - column 11, line 13; figures 1,2,3,4,6 *	1,2,7,8, 12,13,16, 20,23,24, 28	
A	US-A-3 716 373 (D. RHODES) * Claims 1-4; columns 3-4 *	1,17	
D,A	US-A-4 594 258 (R. VITTI et al.) * Claims 1-22; column 4 *	16,17,18	
D,A	US-A-4 594 257 (Y. LEBLANC) * Claims 1-21 *	16,17,19	
A	RESEARCH DISCLOSURE, no. 113, September 1973, disclosure no. 11330; "Light colored agglomerates from spray-dried coffee powder" * Whole article *	4,20	TECHNICAL FIELDS SEARCHED (Int. Cl.5) A 23 F A 23 P
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A	US-A-3 767 419 (B. SIENKIEWICZ et al.)		
A	CA-A-9 241 74 (GENERAL FOODS)		

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	08 January 91	DESMEDT G.R.A.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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(54) **FRUIT CONCENTRATE SWEETENER AND PROCESS OF MANUFACTURE**

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US-A- 2 492 505
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Description

Field of the Invention

The present invention relates to a sweetener composition and process for manufacturing the composition and more particularly to a sweetener composition formed from a fruit juice or fruit syrup concentrate and a corresponding process for manufacture.

Background of the Invention

A number of sweetener compositions and corresponding methods of manufacture have been disclosed in the prior art. Similarly, the prior art has disclosed various products formed from fruits and corresponding methods of manufacture. These prior art products and methods of manufacture are discussed in relative detail below in order to assure an understanding of the present invention. The following discussion deals first with various sweeteners followed by a discussion of fruit products to be distinguished from the present invention.

Significant controversy has developed over the possible deleterious effects of large amounts of sucrose, synthethic sweeteners and refined simple carbohydrates in the human diet. The United States and Europe have recommended modifications in the diet which include a decrease in the uptake of simple sugars, and an increase in complex carbohydrates.

It has also been recommended that sucrose consumption be decreased based on its cariogenic effects and on the significant concern and controversy with regard to the role of dietary sucrose in the etiology of heart disease and diabetes.

Low calorie sweeteners have been used as an alternative to sucrose; however, concern has been expressed with regard to carcinogenic and other potentially hazardous side effects.

Refined sweeteners such as corn syrup, dextrose and fructose have also been used as an alternative to sucrose. However, they are considered "empty" carbohydrate calories because they lack naturally occurring nutritional components such as vitamins, minerals and proteins which are now believed to aid in the digestion of carbohydrates.

Sweetener compositions which are currently known and used as alternatives to sucrose may be divided into three categories. These categories are titled low calorie sweeteners, refined sweeteners and natural or nutritious sweeteners in the following discussion.

Low calorie sweeteners include those sweetening compositions described in Glicksman et al, U.S. Patent 4,001,456; Grosvenor U.S. Patent 3,011,897; Schmitt et al, U.S. Patent 3,653,922 and Fruda et al, U.S. Patent 3,971,857. These sweetening compositions have been prepared by diluting the sweetening power of synthetic sweeteners such as saccharine, cyclamate or dipeptides with dextrose, sucrose, polyglucose, corn syrup solids or maltodextrins.

In an effort to bulk or expand these products to have a volume (but not weight or density) similar to sucrose, various techniques have been employed including dry-blending followed by agglomeration, spray-drying and vacuum drum drying. These products are unique and have the distinct advantage of fewer calories than an equivalent volume of sucrose. Some of these sweeteners, which include bulking agents such as corn syrup solids or maltodextrin in the formulation, also have the advantage of having complex carbohydrates. However, the low bulk density characteristic of these reduced calorie sweeteners also represent a very limited source (less than 0.5g/teaspoon or 5cc) of complex carbohydrates.

Very importantly, the low calorie sweeteners have the disadvantage of containing controversial synthetic sweeteners which also have off-tastes and which decompose under certain food processing conditions. They also have the disadvantage of a substantially lower bulk density than sucrose, thereby excluding their use as a direct substitute for sucrose in many dry food products. Lastly, these low calorie sweeteners are also obviously void of naturally occurring nutritional components such as protein, vitamins and minerals.

The concept of blending refined sugars to produce sweetening composition products which contain reduced amounts of sucrose or no sucrose have been described in Batterman et al, U.S. Patent 4,676,991; Batterman et al, U.S. Patent 4,737,368; McNamara et al, U.S. Patent 3,836,396 and Walon, U.S. Patent 4,049,466. In all of these products, refined fructose has been used to replace or reduce the amount of sucrose.

In the two Batterman et al references, a blend of fructose and sucrose alone was thought to be advantageous because less of the resulting sweetening composition product was required to sweeten foods. This was due to the increased sweetening capacity of fructose which is 1.7 times that of sucrose.

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The McNamara et al reference revealed that a sweetening composition product composed of sucrose, fructose and maltose actually reduced cariogenicity (tooth decay) which has been associated with sucrose alone.

The Walon reference taught that a sweetener composition product can be made by spray-drying a blend of fructose syrup with 50 to 70 weight percent of maltodextrin.

All of the sweetening compositons were reported to be similar in behavior, appearance, sweetness and bulk density when compared with sucrose. The primary disadvantage of these refined sweeteners is that they contained no other nutritional components such as vitamins, minerals and proteins, and for the most part are considered "empty" carbohydrate calories. The water whiteness of the refined sweeteners as in the case of corn syrup, or sucrose dissolved in water, is also considered a disadvantage since the consumer perceives this lack of color as evidence of the deficiency of natural nutritional components.

Also, very recently, there has been some question with regard to the toxicity of fructose because of its metabolic competition with glucose. Consequently, sweetening compositions which contain more than 25% fructose on a solids weight basis have the potential of being deleterious to the individual.

The last category of sweetening compositions which may serve as an alternative to sucrose includes the natural and nutritious sweeteners. Nutritious sweeteners are understood to contain nutritional components such as vitamins, minerals and proteins which occur naturally in addition to the obvious carbodydrate content. These nutritious sweeteners include honey, maple, molasses, cane juice and hydrolyzed whole grain (sorghum, rice and barley) products. The primary disadvantage connected with these natural sweeteners is the distinct flavor associated with them making then undesirable as a substitute for sucrose in many food applications. Another disadvantage is the higher cost of natural sweeteners relative to sucrose making them economically unfeasible for many food applications where sucrose is currently used.

The above mentioned nutritional sweeteners have been available in liquid and solid forms. The solid sweetening compositions made from honey were a combination of fructose, glucose and complex carbohydrates. The complex carbohydrates were added as a drying aid.

Dried molasses also required complex carbohydrates as a drying aid and resulted in a sweetening composition containing glucose, fructose and sucrose (greater than 25% on a dry weight basis) and complex carbohydrates. Maple syrup and cane juice have been dried directly by evaporation techniques and resulted in sweetening compositions primarily comprising sucrose (greater than 75% on a dry weight basis) and residual amounts of fructose glucose. The hydrolyzed whole grain products have also been dried directly by drum or spray drying to result in a sweetening composition including a combination of glucose, maltose and complex carbohydrates.

All of the above mentioned nutritional sweeteners contain at least about 0.5% by weight combined protein, vitamins and minerals and are usually colored as opposed to the whiteness of refined sucrose or the water whiteness of corn syrup. This relatively small percentage of nutritional components has been considered by some to be essential in the digestion and subsequent metabolism of carbohydrates.

Lately, there has been a tremendous surge of products which incorporate fruit juice, especially in products such as soft drinks. These products have been well received by the health conscious consumers. Fruit juice concentrates and, more recently, powdered fruit juice have been used as commercial items of trade to impart desirable flavors as well as some sweetness to these products.

Fruit juice concentrates are deficient in complex carbohydrates but do have a natural balance of fructose, glucose and sucrose and nutritional components such as vitamins, minerals and proteins. The primary difference between fruit juice and fruit juice concentrate is that the latter has been depectinized so as to allow concentration to at least 40% and preferably to 60 or 72% soluble solids without gelation.

The fruit juice concentrates provide economical benefits for reducing shipping costs by not having to transport unnecessary water weight. Unfortunately, these have a very limited shelf life unless refrigerated or frozen. Consequently, it is difficult and costly for many manufacturers to use these fruit products because of the necessary refrigerated storage conditions.

Further concentration to about 78% soluble solids of the 60 to 72% fruit juice concentrates results in a significantly more stable product which does not need refrigeration. However, undesirable browning and flavor alterations have been found to result from this concentration and to preclude its use.

Use of juice concentrates with less than 72% soluble solids, in food product formulations, has been severely limited due to their functional inability to be substituted on a 1:1 basis for corn syrup of approximately 80% soluble solids (the ingredient they are most likely replacing).

The flavor associated with these fruit juice concentrates of less than 72% soluble solids has also restricted their usage as a sweetener alternative for liquid sucrose or corn syrup. So called "deflavorized," "decolorized" and even "reduced acid" juice concentrates can be made from any clear fruit juice concentrate and have been made available commercially. "Fruit syrup concentrates" (as opposed to "fruit

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juice concentrates") are juice concentrates (thus depectinized) which are processed through a separate ion exchange system resulting in substantially reduced flavor, color, acid and nutrients. However, some of these concentrates, and particularly pineapple, pear and mixed fruit, still exhibited significant color and fruit flavor identification, thus limiting their application.

The flavor associated with these fruit juice concentrates or fruit syrup concentrates, their poor storage stability, their physical and functional inability to be directly substituted for corn syrup or liquid sucrose in food formulations other than liquid beverages, and their high cost relative to sucrose or corn syrup have restricted their usage as an alternative sweetener. This is exemplified by the common use of fruit juice concentrates predominantly in the beverage industry at less than 10% by weight reconsituted juice, the primary sweetness being derived from alternative sources such as corn syrup products, artificial sweeteners, or sucrose.

Powdered fruit juices have been described in the literature for the purpose of preserving the fruit juice for later reconstitution with water and more specifically preserving the flavor material as well as the nutritional components. Because of the difficulties found in drying these juices which contain fructose, glucose and sucrose, as well as vitamins, minerals and proteins, a variety of different drying aids have been used. Hunter et al, U.S. Patent 4,537,637 and Gupta et al, U.S. Patent 3.953,615 disclosed hydration drying of fruit juice by the use of anhydrous alpha-glucose. Kern, U.S. Patent 1,204,880 taught the use of insoluble cellulose fiber to dry and preserve fruit juice. Lee, U.S. Patent 2,453,142 disclosed the use of hemicellulose xylan and calcium bearing phytates to dry and preserve fruit juice.

Gupta, U.S. Patent 4,112,130; Stern, U.S. Patent 3,483,032 and Fleming, U.S. Patent 1,361,238 taught the use of hydrolyzed starch for the preservation of fruit juices with their flavors and natural nutritional components.

The Fleming reference specifically disclosed the use of hydrolyzed starch containing glucose, maltose and approximately 50% dextrin, for the drying of the 100% pure unconcentrated fruit juice. The Stern reference taught that 100% pure unconcentrated fruit juices could be readily dried using corn syrup solids in combination with lactose. The Gupta reference taught the use of solid maltodextrin for the drying of 100% pure orange juice. It was found in these latter patents that dried hydrolyzed starch products having a dextrose equivalent (D.E.) of less than 20 (by definition, hydrolyzed starch products of less than 20 D.E. may also be termed maltodextrins) were particularly effective as a drying aid for 100% pure fruit juices. By 1970, dried maltodextrin was a commercial item of trade. Liquid maltodextrin, on the other hand, has not been readily available due to its instability at 70% soluble solids and its extremently high viscosity even at 70% soluble solids, making handling of this raw material very difficult. Consequently, dried maltodextrin as opposed to the syrup form has been the preferred ingredient as indicated, for example, by its usage in the Gupta and Stern references noted above. The preparation and use of maltodextrin as a drying aid have been described in Horn et al, U.S. Patent 3,826,857; Harjes et al, U.S. Patent 3,974,033 and the Walon reference noted above. Accordingly, those references as well as the other U.S. Patents discussed herein are incorporated by reference to the extent that they will facilitate a better understanding of the present invention.

The aforementioned powdered fruit juices are used primarily for flavoring and/or reconstitution to liquid fruit juice beverages. In all of the above cases, the object of drying the fruit juices necessitated the preservation of the flavor material as well as the nutritional components.

Denny, U.S. Patent 1,746,994 and Bartz, U.S. Patent 2,525,761 taught the deflavorization of raisin syrup and fruit juice respectively.

In the Denny reference, a syrup was made from raisins (as opposed to the whole fruit) and deflavorized by physical concentration of the extracted raisin liquor to 60o Brix and removal of crystallized tartrate compounds followed by treatment with lime which reportedly removed the residual tartrate compounds along with tannins and some color and flavor materials. Carbon was used to complete the removal of any residual color in the syrup.

The Bartz reference taught that fruit juices could be deflavorized, thereby producing mono- and di-saccharides sugars, liquid sugar and edible syrups. Unfortunately, the process claimed involved depectinization followed by chemical deflavorization via the addition of basic salts (aluminum, barium, strontium and preferably lead were given as examples). This was followed by the subsequent removal of divalent metallic elements as insoluble oxalates. Carbon was used primarily and essentially to remove all the color material to produce a water white liquor as well as removing "any remaining bitter principles and lead salts", thus indicating the use of carbon primarily for decolorization and secondarily for deflavorization purposes. It is understood that residual concentrations of the basic salts in parts per million (ppm) would exist in the finished product so that these basic salts would be contaminants additionally distinguishing the product.

It was also claimed that the water white liquor product of this invention could be spray dried directly (without the use of drying aids) to produce a product in solid form.

A variety of drying techniques have been used in making powdered fruit juices. These include spray drying at relatively low temperatures to preserve flavor and nutritional components, vacuum drum drying, rotary vacuum drying, and a relatively new method involving extrusion drying into a relatively cool solvent such as isopropyl alcohol.

Thus, although a wide variety of sweeteners have been made available in the prior art, there has been found to remain a need for a sweetener composition or compositions having improved, enhanced and novel characteristics as defined in greater detail below.

Summary of the Invention

Accordingly, it is an object of the present invention to provide an improved fruit concentrate sweetener composition and process of manufacture for overcoming one or more disadvantages discussed above in connection with the prior art.

More particularly, it is a method of the present invention to provide a fruit concentrate sweetener composition and process of manufacture wherein the sweetener composition is formed as a blend of hydrolyzed starch having a dextrose equivalent (D.E.) of up to about 25 and a fruit juice or fruit syrup concentrate of at least about 40% soluble solids and aobut 0% insoluble solids to form a liquor having a dry weight composition of 40 to 65% complex carbohydrates, 35 to 55% simple sugars from the fruit juice or fruit syrup concentrate and 0 to 5% nutritional components.

The fruit concentrate sweetener composition referred to above may contain natural flavor components from its fruit origin. However, the fruit concentrate sweetener composition is preferably substantially completely deflavorized or more preferably substantially completely deflavorized in order to form a bland sweetener product which can be directly substituted for prior art sweeteners such as granular or powdered sucrose, corn syrup and the like.

It is a corresponding object of the invention to provide the fruit concentrate sweetener composition and process for manufacture as described above wherein the sweetener composition is preferably dried to 78 to 80% soluble solids to make the sweetener composition suitable for replacing corn syrup and the like or to dry the product to 96 to 99% soluble solids to make the sweetener composition suitable for replacing powdered or granulated sucrose and like sweeteners.

Even more preferably, the dry fruit concentrate sweetener composition may be compacted in order to provide a bulk density substantially identical to the bulk density of the replaced sweetener.

In accordance with the object summarized above, the present invention provides a novel fruit concentrate sweetener composition and process of manufacture which can be employed as an alternative for conventional sweeteners such as sucrose, corn syrup and the like. At the same time, the fruit concentrate sweetener composition of the present invention is also novel in having all of the following qualifications as a sweetener product:

(1) The sweetener composition is derived from a natural source and preferably contains many if not substantially all of the nutritional components of the sweetener origin including vitamins, minerals proteins as well as a natural combination of simple sugars such as glucose, fructose and sucrose from the fruit origin;

(2) The sweetener composition also has a significant quantity of complex carbohydrates (in excess of 1.5 grams/teaspoon or 5cc.) which greatly enhance the nutritional value of the sweetener compostion;

(3) The sweetener composition has been found to have a sweetening power and bulk density similar to that of sucrose so that the sweetener composition may be substituted substantially on a weight-for-weight basis for sucrose in most sweetened food products and beverage products;

(4) The sweetener composition, upon consumption, reduces the intake of simple sugars by approximately 50% with a corresponding increase in the intake of complex carbohydrates as compared, for example, to a conventional sweetener such as sucrose, because of the components of the sweetener composition as summarized above;

(5) The sweetener composition, at least in a preferred form, has a bland, clean flavor identifible with that of refined sugar, for example;

(6) The sweetener composition is completely soluble with a rate of solution comparable to that of sucrose; and

(7) The sweetener composition is relatively economical.

Thus, it is yet a further object of the invention to provide a unique and novel sweetening composition and process of manufacture capable of fulfilling all of the above criteria. As for the sweetener composition

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being economical, a direct comparison with existing sweeteners such as sucrose, corn syrup and the like naturally will depend on a large number of factors. However, the sweetener composition of the invention is believed to be economical in the sense referred to above in that it is produced from a widely available source, namely a wide variety of fruits, and by processing techniques facilitating its manufacture.

It is yet a further object of the invention to provide various sweetened food and beverage products including the sweetener composition of the present invention as a basic component. Preferably, because of the characteristics of the sweetener composition as noted above, it may be substituted directly into most sweetened food and beverage products on a direct weight-for-weight basis compared to such conventional sweeteners.

It is still a further object of the invention to provide an improved process of manufacture for the sweetener composition of the invention. For example, the hydrolyzed starch component of the initial liquor blend preferably has a dextrose equivalent (D.E.) in the range of 5 to 25, more preferably being a maltodextrin of 5 to 15, and also more preferably comprising 30 to 40% soluble solids prior to the maltodextrin being blended with the fruit juice or fruit syrup concentrate. The fruit juice or fruit syrup concentrate preferably comprises at least 65 to 72% soluble solids. At the same time, the fruit juice or fruit syrup concentrate is employed in a clear condition indicating that it has about 0% insoluble solids.

The blending of the maltodextrin and fruit juice or fruit syrup concentrate as discussed above has been found not only to provide the unique combination of high sweetness and complex carbohydrate content but also facilitates both deflavorization and drying of the resulting sweetener composition in accordance with the present invention.

In accordance with the preceding summary, it is a basic object of the invention to provide a fruit concentrate sweetener composition consisting essentially of a dry weight composition of 40 to 65% complex carbohydrates, 35 to 55% simple sugars of a fruit origin, about 0% insoluble solids, 0 to 5% nutritional components and 0 to 3% of a sweetness potentiator, the balance of the sweetener composition being essentially water.

The sweetener composition summarized immediately above may be modified in substantially the same ways discussed above to form a wide variety of products icnlduign an initial liquor, a partially dried product of 78 to 80% soluble solids or a substantially dried product having 96 to 99% solids. At the same time, the sweetener composition preferably includes natural nutritional components from the fruit origin but may, if desired, have those nutritional components either removed or fortified. Still further, the sweetener composition of the present invention may be enhanced by additon of a sweetness potentiator added to enhance the sweetness of the sweetener composition as described in greater detail below.

Additional objects and advantages of the invention are made apparent in the following description.

Detailed Description of the Preferred Embodiments

The sweetener composition of this invention is a blend of hydrolyzed starch of less than 25 D.E. with a clear fruit juice concentrate or fruit syrup concentrate of greater than 40% soluble solids. The above blend having a dry weight composition of 40% to 65% complex carbohydrates, 35 to 55% simple sugars derived from the fruit juice concentrate or fruit syrup concentrate and 0 to 5% nutritional components.

We found that hydrolyzed starch of less than 25 D.E. proved to be a very good drying aid as well as being an excellent source of complex carbohydrates. While commercially dried maltodextrins having a D.E. of less than 20 are available and would be the most logical to use since it is more practical to remove as little water as is absolutely necessary in the drying process, we found that its poor dissolvability from a manufacturing standpoint made its usage not only impractical but also non-economical. Liquid maltodextrin has been found to be more desirable from a blending point of view, although it is not readily available as a commercial item.

We found that by making the maltodextrin from starch by means of acid or enzyme and more preferably by bacterial amylase on a 30 to 40% dry substance basis (DSB) water/starch slurry, the maltodextrin formed had a D.E. of about 5 and a superior drying capacity. Starch hydrolsates having a D.E. of between 15 and 25 could also be used as a drying aid and source of complex carbohydrates in the said sweetener composition. However, the resulting sweetener composition products were slightly more hygroscopic than those products made with hydrolyzed starch of less than 15 D.E. This was presumed to be a consequence of the glucose and maltose which tended to contribute toward hygroscopicity in the final product.

We found it critical to keep the combined percentage of these simple sugars contributed by the hydrolyzed starch to the sweetening composition at below 10% and preferably less than 5%. We also found that centrifugal and/or filtration of the hydrolyzed starch liquor removes many of the bitter components

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associated with the liquor which otherwise detracted from the sweetness of the fruit juice concentrate when combined with the hydrolyzed starch.

Clear fruit juice concentrates may contain on a dry basis up to about 5% nutritional components such as vitamins, minerals and proteins, as opposed to fruit syrup concentrates which contain less and sometimes none at all. When the above concentrates were used to make the fruit concentrate sweetener composition, the product which resulted contained anywhere from 0 to 3% total nutritional components on a dry weight basis. We found that in some cases it was desirable to fortify the nutritional components by the addition of protein, vitamins and minerals so as to obtain a sweetening composition having up to 5% nutritional components on a dry weight basis.

Fruit juice concentrates and/or fruit syrup concentrates such as grape, pineapple, apple, pear and mixed fruit are examples of clear fruit concentrates which are commerical items of trade. Approximately 95% or more of their total soluble solids are a combination of simple sugars including glucose, fructose, sucrose and, most notably in the case of pear, sorbitol. These concentrates may also contain up to 5% nutritional components and 0% insoluble solids. Regardless of the fruit source of the concentrate, the resulting sweetener composition as described in this invention contained less than 27% fructose or sucrose.

The fruit concentrates are prepared from fruit juices by depectinization followed by concentration greater than 40% and usually between 60 and 72% soluble solids. Prior to concentration, the clear fruit juices may be subject to decolorization and deflavorization by activated carbon and possibly acid reduction by deionizing techniques. While these concentrates are described as having reduced acid, color and flavor, we found them and particularly the pineapple concentrate to still possess significant fruit flavor identification and referred to them as being partially deflavorized. Depending on the application of the fruit concentrate sweetener composition, the flavor resulting from concentrates being used may or may not be acceptable. Therefore, we considered a substantially completely deflavorized version of the product to be used in those applications where the effective absence of fruit flavor identification is critical.

Flavor profiles of products are usually complex chemical compositions which are not fully identifiable by analytical methods. The classic example of this is coffee which has been extensively analyzed and yet never successfully reproduced by synthetically combining the flavor constitutents. Likewise, it is very difficult to determine the flavor profile of the fruit concentrates by chemical analytical techniques.

However, we did find that the method developed at Arthur D. Little, Inc. for determining flavor profile worked very well. Essentially, five trained persons functioned as a unit under the direction of a panel leader and produced a verbal description of the product. The flavor complex was described in terms of character notes, intensity, order of appearance, after-taste and amplitude. The panelists evaluated the products independently and then discussed results to arrive at common opinions. This method was used to evaluate the flavor of the fruit juice concentrates, the fruit syrup concentrates, the fruit concentrate sweetening compositions of this invention and products made with the said sweetening composition.

We found that the deflavorized fruit juice concentrates or fruit syrup concentrates of white grape, pear and apple contained the least flavor identification while pineapple contained the most. At the same time, we also found the pineapple to be the most desirable from both an economical and product point of view.

Economically, pineapple concentrate is the least expensive of the aforementioned fruit concentrates and the most consistent in supply and price. The pineapple concentrate also possesses a desirable blend of glucose, fructose and sucrose, which we found to significantly aid in the drying process and the functionality of the fruit concentrate sweetener composition. However, as mentioned above, the fruit juice concentrates and fruit syrup concentrates particularly from pineapple, even though they may have been deflavorized and decolorized by activated carbon and even deionized to reduce acid, still possessed significant flavor identification.

To our surprise, we found that diluting the fruit concentrate of 63 to 72% soluble solids with a hydrolyzed starch of less than 25 D.E. and of 30 to 40% dry substance basis to yield a sweet liquor of 38 to 52% soluble solids having been only partially deflavorized with a flavor resembling that of the fruit concentrate being used, and subsequently treating this liquor with activated carbon for a limited time, that a substantially completely deflavorized liquor was obtained which was not necessarily totally decolorized.

We also found that the activated carbon also removed any remaining bitter notes derived from the hydrolyzed starch. Importantly, we found that no chemical agents were necessary to affect deflavorization and that physical adsorption by activated carbon under the conditions noted above were sufficient.

In fact, to our amazement, we also found a significant increase of 25% in relative sweetness between the liquor treated with activated carbon as described above, and an equivalent blend of refined fructose, glucose, sucrose and maltodextrin. Presumably, this additional sweetness of the fruit concentrate sweetener composition, as compared with the equivalent refined blend, is due to the natural nutritional components contained in the fruit concentrates.

We found that, after our treatment of the blended liquor with activated carbon, any of the fruit concentrates mentioned above could be used satisfactorily alone or in combination to yield a bland tasting fruit concentrate sweetener composition having no fruit flavor identification. The sweetness associated with those fruit concentrate sweetener compositions were found to be on the order of 0.8 that of sucrose. In food formulations where the sweetener constitutes greater than 30% of the total formulation,. we found that there did not exist a significant difference in perceived sweetness. However, we found that, by adding a natural or synthetic sweetness potentiator such as stevicoside, saccharine, dipeptides, etc., at levels less than 3% and preferably less than 1% of the total soluble solids, the resulting sweetening composition had a sweetness equivalent to, or slightly exceeding sucrose. These fruit concentrate sweetener compositions containing a natural or synthetic sweetness potentiator at levels less than 3% were found to be beneficial in applications where low levels of sweetener (particularly less than 10%) were used.

Fruit concentrates are normally only concentrated to between 60 and 72% soluble solids because further concentration results in flavor degradation, browning and carmelization. Unexpectedly, it was found that the fruit concentration sweetener composition of this invention could be concentrated up to 80% soluble solids under vacuum at less than 70 °C and more preferably at 60 °C without flavor degradation or browning of the product.

With greater than 78% soluble solids, the product requires no refrigeration and for the most part is microbiologically stable due to the reduced water activity and osmotic pressure of the product. It was further found that this 78% fruit concentrate sweetener composition and particularly the deflavorized version, could readily be used to replace corn syrup on a 1:1 basis in many food applications including confectionary systems.

The sweetening composition of this invention, when substituted for corn syrup in many food formulations, was found to contribute similar mouthfeel and textural properties to food products normally obtained with corn syrup. Importantly from a manufacturing point of view, the fruit concentrate sweetening composition of 78 to 80% soluble solids also had a viscosity which was similar to corn syrup of 78 to 80% soluble solids. It was presumed that many of these textural and functional advantages as well as the ability of the fruit concentrate sweetening composition to be concentrated satisfactorily to 80% soluble solids, was a consequence of the presence of the complex carbohydrates from the hydrolyzed starch.

It was also found that the fruit concentrate sweetener composition (as opposed to fruit juice concentrate or fruit syrup concentrate) could be dried to between 96% and 99% soluble solids by most of the standard drying techniques including spray drying, drum-drying, freeze drying, foam-mat drying, rotary vacuum drying and extrusion drying. The dried product has a substantially lower hygroscopic nature than a dried fruit juice concentrate or fruit syrup concentrate alone, which has never really been achieved successfully anyway because of the hygroscopic nature of the dried fruit juice concentrate.

When natural components such as vitamins, minerals and proteins are present, it was additionally important to dry the product at substantially lower temperatures to preserve the nature of these components. However, it is also essential to maintain lower temperatures for many of the drying techniques discussed below to be lower than the melting point of the sweetening composition. The most preferred methods of drying are spray drying, drum-drying and rotary vacuum drying.

For spray drying purposes, it has been found that if the fruit concentrate sweetener composition is diluted with water to adjust the soluble solids to between 35 and 45% soluble solids, the liquor may be dried via spray drying with a centrifugal atomizer at 15,000 to 22,000 revolutions per minute (rpm), an inlet temperature of between 105 °C and 205 °C and an outlet temperature of between 70 °C and 90 °C.

If the liquor is in excess of 45% soluble solids, we have found that the product does not atomize sufficiently to affect adequate drying and the material sticks to the walls of the dryer. At concentrations less than 35% soluble solids, the amount of water that would have to be removed would significantly increase the cost of drying the product to prevent the product from being economically competitive with sucrose.

We also have found that it is very important that the temperature of the liquor entering the spray dryer not exceed 70 °C. Temperatures above the point result in an increased feed rate to the spray machine causing a "wetting" out of the chamber walls which does not happen under the same conditions with a liquor temperature of less than 70 °C. Liquor temperatures under 38 °C are avoided because they tend to decrease the efficiency of the dryer as well as the atomizer capability. It is essential that the dried product temperature not exceed 62 °C as it then starts to melt and stick to the walls of the chamber.

The overall rate of drying is a function of air flow and subsequently the humidity in the chamber. Due to the hygroscopic nature of the product material, it has been found that the product reluctantly releases moisture on drying and re-absorbs water rapidly in high humidity conditions. Hence, air supplied to the dryer is preferably dehumidified and supplied at such a rate so that the relative humidity is below that causing the product to become tacky. Also, the small size of the particle provided by the atomizer is

essential to allow for easy release of the water being held by the product.

A different set of conditions has been found to be necessary for the sweetening composition when vacuum drying techniques were employed.

When vacuum drum-drying, the fruit concentrate sweetening composition for economical purposes is first concentrated udner vacuum up to 80% soluble solids before being applied to the drums. The material is dried under vacuum at less than 70 °C. Rotary vacuum drying is preferably accomplished in less than 30 seconds at temperatures of appoximately 130 °C under vacuum to concentrate the fruit concetrate sweetening composition up to 99% soluble solids. The resulting molten galss is then deposited into chilled rolls and flaked off resulting in particles of mesh sizes varying from 4 to 250 mesh. The particles are then classified to yield products of large and small mesh sizes for granular and powdered purposes.

It has been found that the fruit concentrate sweetening composition of up to 80% soluble solids may also be atmosoherically drum dried. The product resulting from this operation is thermoplastic and cooled to form a glass which may be milled to the appropriate size. Unexpectedly, the product has been found to be much less hygroscopic than the product obtained from spray drying. The atmospherically drum dried product is brown in color and has a caramel flavor presumably resulting from the browning Maillard reaction. However, lower temperatures of approximately 105 °C, and special application of the sweetening composition to the drums, have resulted in a very acceptable product being only slightly beige in color and having very little detectable off flavors. Upon grinding, the resulting granular crystals are relatively less hygroscopic than the spray dried powder and are very similar to sucrose in appearance and taste, having a bulk density of 0.85g/cc.

The density of the dried fruit concentrate sweetener composition, with up to 00% soluble solids, has been found to be in the range of 0.7 to 0.85g/cc while that of sucrose is 0.80 to 0.90g/cc. The dried sweetener composition may also be densified if desired by slight compression through two rolls followed by grinding and sifting. The density of the resulting material is then between 0.8 and 0.9g/cc.

The solubility of the dried fruit concentrate sweetening composition is similar to that of granulated sucrose, a 10% solution being totally dissolved in water within 30 seconds. Clumping caused by "wetting" of the composition powder may be alleviated by the addition of a dispersibility agent such as silicon dioxide at a level less than 2% weight/weight of the dried sweetener composition.

Overall, it has been found to our surprise that clear natural fruit concentrates or fruit syrup concentrates having a combination of simple sugars such as glucose, fructose and sucrose, with or without other nutritional components and upon being blended with hydrolyzed starch of less than 25 D.E., results in a sweetener composition having unique funcitonal and sweetening properties as well as valuable dietary nutritional advantages.

The dry weight composition of these sweetener compositions contains anywhere from 40 to 65% complex carbohydrates derived from the hydrolyzed starch. 35 to 55% simple sugars in the sweetening composition are derived from the fruit juice concentrate or fruit syrup concentrate. This relationship between simple and complex sugars is decidedly advantageous from a nutritional guideline standpoint since food products made with the sweetener composition of this invention, as a replacement for sucrose, reduces by approximately 50% the simple sugars and increases by approximately 50% the complex carbohydrates being consumed.

Importantly, the sweetener composition may also be substantially completely deflavorized if desired to avoid any flavor associated with its fruit source thereby resulting in a bland tasting product having taste characteristics similar to refined sweeteners such as sucrose and corn syrup. Very notably, the powdered or granular form of the sweetener composition product, having 96 to 99% soluble solids, has the bulk density, solubility and sweetness characteristics of sucrose. The sweetener composition of this invention may also be concentrated up to 80% soluble solids to form a stable product having textural and functional properties similar to corn syrup. It may thus be substituted for corn syrup on a 1:1 basis in most food formulations.

Lastly, from an economical point of view, blending of the relatively inexpensive corn starch which was hydrolyzed on site prior to mixing with the fruit concentrate, produced a natural fruit concentrate sweetener composition which was considerably less expensive, more stable and having more food products application than the original fruit concentrate.

Thus, the present invention provides a novel fruit concentrate sweetener composition and process for manufacture in accordance with the preceding summary and description. Further preferred details of both the sweetener composition and process of manufacture are made apparent in the following examples.

EXAMPLE I

Preparation of a Hydrolyzed Starch by Enzyme Conversion

An aqueous starch slurry was prepared by blending modified corn starch weighing between 170 and 270Kg into 340Kg water in a swept surface steam jacketed kettle. A bacterial alpha-amylase (Tenase 1200, a product of Miles Chemical Laboratories) in an amount of about 0.34% was then added and the slurry slowly heated over a period of time up to an hour to approximately 77°C. The enzyme conversion was allowed to continue until the desired dextrose equivalent was reached. The temperature of the liquor was then quickly raised to 120°C to inactivate the enzyme and terminate the conversion. The hot liquor was immediately centrifuged and/or filtered. The starch hydrolysates thus prepared were between 30 and 40% soluble solids and had a D.E. of between 5 and 25.

EXAMPLE II

Preparation of a Hydrolyzed Starch by Acid-Enzyme Conversion

An aqueous starch slurry was prepared by blending modified corn starch weighing between 170 and 270Kg into 340Kg water in a swept surface steam jacketed kettle. The slurry was then partially acid hydrolyzed to a D.E. of between about 10 and 15. The pH of the acid hydrolyzed slurry was then adjusted to between 6 and 7. A bacterial alpha-amylase (Tenase 1200, a product of Miles Chemical Laboratories) in an amount of 0.04% was then added to the slurry at about 75°C. The slurry was kept at that temperature for approximately one to two hours to result in the desired starch hydrolysate of this invention before being brought to 120°C to inactivate the enzyme. After liquefaction was complete, the hydrolyzed starch liquor of between 30 and 40% soluble solids and between 15 and 25 D.E. was centrifuged and/or filtered.

Examples I and II disclose the preferred methods for forming a hydrolyzed starch component of the sweetener composition according to the present invention. However, these examples are merely illustrative of techniques for forming the hydrolyzed starch component. It is to be understood that other methods of manufacture may be employed as long as the hydrolyzed starch component is in the form of maltodextrin having the dextrose equivalent values recited for the present invention and preferably having between about 30 and 40% soluble solids prior to being blended with a clear fruit juice or fruit syrup concentrate according to the present invention. These characteristics for the hydrolyzed starch are necessary in the present invention to provide the complex carbohydrate composition for the sweetener product and also to facilitate both deflavorization and drying of the sweetener product.

EXAMPLE III

Preparation of a Flavored Pineapple Concentrate Sweetener Composition

A clear pineapple juice concentrate of 40% soluble solids (50 weight percent on a dry basis) was blended with a hydrolyzed starch of 25 D.E. and 40% soluble solids (50 weight percent on a dry bsis). The resulting sweetener composition of 40% soluble solids (50 weight percent on a dry basis). The resulting sweetener composition of 40% soluble solids, had a strong and distinct pineapple flavor and the following percent by weight dry substance analysis:

Glucose	11.2%
Fructose	12.0%
Sucrose	25.1%
Maltose	5.8%
Complex Carbohydrates	43.0%
Nutritional Components (protein, vitamins and minerals)	2.9%

EXAMPLE IV

Preparation of a Partially Deflavorized Pineapple Concentrate Sweetener Composition

A clear deodorized and deflavorized pineapple juice concentrate (product of Gamma Foods, Wapato, Washington), of 70% soluble solids (50 weight percent on a dry basis) was blended with a hydrolyzed starch of 10 D.E. and 30% soluble solids (50 weight percent on a dry basis). The resulting sweetener composition of 42% soluble solids, had a slight but distinct pineapple flavor and the following percent by weight dry substance analysis:

Glucose	10.2%
Fructose	13.0%
Sucrose	26.5%
Maltose	1.7%
Complex Carbohydrates	48.1%
Nutritional Components (protein, vitamins and minerals)	0.5%

EXAMPLE V

Preparation of a Completely Deflavorized Pineapple Concentrate Sweetener Composition

A clear pineapple syrup concentrate (Ionex pineapple syrup concentrate from Dole Processed Foods) of 72% soluble solids (35 weight percent on a dry basis) was blended with a hydrolyzed starch of 5 D.E. and 30% soluble solids (65 weight percent on a dry basis). The combined sweetener composition of 38% soluble solids, had a slight but distinct pineapple flavor. The sweetener composition was then passed through a chamber containing activated granular carbon (CAL 12 X 40 a product of Calgon Carbon Corporation) with a residence time of approximately 30 minutes. The substantially completely deflavorized, beige liquor had the following percent by weight dry substance analysis:

Glucose	7.5%
Fructose	9.0%
Sucrose	18.0%
Maltose	0.7%
Complex Carbohydrates	64.3%
Nutritional Components (protein, vitamins and minerals)	0.5%

EXAMPLE VI

Preparation of a Completely Deflavorized Grape Concentrate Sweetener Composition

A clear grape juice concentrate of 72% soluble solids (50 weight percent on a dry basis) having been deflavorized, decolorized and deionized, was blended with a hydrolyzed starch of 5 D.E. and 40% soluble solids (50 weight percent on a dry basis). The resulting partially deflavorized grape concentrate sweetener composition of 51% soluble solids, still had a very slight fruity flavor and distinctly beige color associated with it. The partially deflavorized sweetener composition was then passed through a chamber containing activated carbon with a residence time of up to two hours. The substantially completely deflavorized and decolorized grape concentrate sweetener composition had the following percent by weight dry substance analysis:

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Glucose	27.0%
Fructose	22.1%
Sucrose	1.0%
Maltose	0.6%
Complex Carbohydrates	49.3%
Nutritional Components (protein, vitamins and minerals)	0%

EXAMPLE VII

Preparation of a Completely Deflavorized, Nutritionally Fortified, Mixed Fruit Concentrate Sweetener Composition

A clear pineapple juice concentrate of 72% soluble solids and a clear grape juice concentrate of 70% soluble solids, both having been deflavorized, decolorized and deionized, were blended at a 50 to 50 dry substance basis to make a mixed fruit concentrate of about 71% soluble solids. This mixed fruit concentrate (50 weight percent on a dry basis) was then blended with a hydrolyzed starch of 5 D.E. and 35% soluble solids (50 weight percent on a dry basis). The resulting sweetener composition of 46% soluble solids, was considered to be partially deflavorized having a slight fruity flavor identified as pineapple. This partially deflavorized mixed fruit sweetener compositon was then passed through a chamber containing activated carbon with a residence time of approximately 60 minutes. The completely deflavorized sweetener composition had the following percent by weight dry substance analysis:

Glucose	18.4%
Fructose	17.3%
Sucrose	13.0%
Maltose	0.8%
Complex Carbohydrates	49.9%
Nutritional Components (protein, vitamins and minerals)	0.6%

To the above sweetening composition was added water soluble protein, vitamins and minerals so as to contain 5% nutritional components.

Examples II through VII illustrate various types of fruit juice or fruit syrup concentrates which can be employed in accordance with the present invention for blending with the hydrolyzed starch component to form the sweetener composition of the present invention. As noted above, the fruit juice or fruit syrup concentrate is always initially clear, corresponding with the additional requirement that both the fruit juice or fruit syrup concentrate is always initially clear, corresponding with the additional requirement that both the fruit juice or fruit syrup concentrate and the resulting sweetener composition have approximately 0% insoluble solids.

These examples further illustrate that the preferred form of the clear fruit juice or fruit syrup concentrate, upon combination with the hydrolyzed starch component, can also facilitate deflavorization and drying of the resulting sweetener composition.

More preferably, the resulting sweetener composition is also seen to include natural nutritional components from the fruit juice or fruit syrup concentrate.

EXAMPLE VIII

Preparation of a Fruit Concentrate Sweetener Composition Containing a Natural Sweetening Potentiator

A sweetener composition similar to that described in Example V above but additionally containing 3% of the dried and finely ground (200 mesh) leaves of the stevia rebaudiana plant. The potential sweetener composition of this example was found to have sweetness greater than sucrose.

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EXAMPLE IX

Preparation of a Fruit Concentrate Sweetener Composition Containing a Synthetic Sweetening Potentiator

A sweetener composition similar to Example IV above but also containing saccharin at a level of 0.04% dry substance basis to produce a sweetener composition had a sweetness greater than sucrose.

Examples VIII and IX merely indicate that the sweetener composition of the present invention may be further enhanced by the addition of either a natural or synthetic sweetening potentiator. The effect of the sweetening potentiator is to increase sweetness of the sweetner composition to a level greater than that for conventional sweeteners such as sucrose, corn syrup or the like. As noted elsewhere, such a potentiated sweetener composition according to the present invention is useful in various sweetened food and beverage products, particularly those products having a relatively low percentage of sweetener component.

EXAMPLE X

Preparation of an 80% Soluble Solids Fruit Concentrate Sweetener Composition

The sweetener composition of Example V was concentrated under vacuum at 60 °C to a slightly beige syrup having a viscosity of approximately 100 Poises at 37 °C. The product was stored at ambient temperature for 3 months with no indication of microbial instability.

EXAMPLE XI

Preparation of an 78% Soluble Solids Fruit Concentrate Sweetener Composition

The sweetener composition of Example VI was concentrated under vacuum at 70 °C to a colorless syrup having a viscosity of approximately 90 Poises at 37 °C. The product was stored at ambient temperature for 3 months with no indication of microbial instability.

Examples X and XI demonstrate that a sweetener composition produced in accordance with the present invention can be stored even at ambient conditions for extended periods of time without microbial instability.

These examples further demonstrate the relative ease with which the sweetener composition can be concentrated to approximately 80% soluble solids in order to form a syrup type sweetener suitable, for example, for direct replacement of sweeteners such as corn syrup and the like.

EXAMPLE XII

Preparation of a Spray Dried Fruit Concentrate Sweetener Composition

The fruit concentrate sweetener composition of Example III was diluted with water to 35% soluble solids and the temperature of the in-going liquor composition was adjusted to 38 °C. The centrifugal atomizer was set at 22,000 rpm and the dryer set at an inlet temperature of 105 °C and an outlet temperature of 70 °C. Two percent dry weight Syloid Silica (silicon dioxide) was added to the product cooling tubes. The white amorphous powder of between 100 and 200 mesh contained 1.8% moisture and had a density of 0.7g/cc. The product was found to be completely soluble in water at 10% soluble solids at a time within 30 seconds.

EXAMPLE XIII

Preparation of a Spray Dried Fruit Concentrate Sweetener Composition

The fruit concentrate sweetener composition of Example VI was diluted with water to 45% soluble solids and the temperature of the in-going liquor compositon was adjusted to 70 °C. The centrifugal atomizer was set at 15,000 rpm and the dryer set at an inlet temperature of 205 °C and an outlet temperature of 90 °C. Approximately 1% Syloid Silica (silicon dioxide) was added to the product in the cooling tubes. The dried product of less than 62° C was a white amorphous powder of between 50 and 150 mesh and having a moisture content of approximately 2.7%.

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EXAMPLE XIV

Preparation of Vacuum Dried Fruit Concentrate Sweetener Composition

A fruit concentrate sweetener composition of Example V was vacuum drum dried at a drum temperature of less than 70°C resulting in a flaky white sheet of 96% soluble solids.

EXAMPLE XV

Preparation of Rotary Vacuum Dried Fruit Concentrate Sweetener Composition

The fruit concentrate sweetener composition of Example V was evaporated to dryness of 98% soluble solids at a temperature of 65°C by using a rotary vacuum to concentrate the liquor and then deposit it at 98% soluble solids onto chilled flaker rolls. The dried product was of varying mesh sizes of from 4 to 250 mesh which were then air classified to make a relatively granular form of the dried sweetener composition as well as a powder form of the composition. The density of the product was found to be approximately 0.85g/cc.

EXAMPLE XVI

Preparation of an Atmospherically Drum-Dried Fruit Concentrate Sweetener Composition

The sweetener composition of Example V was atmospherically drum dried at 105°C to produce a melted glass of 99% soluble solids which dried rapidly upon cooling and was relatively non-hygroscopic after grinding. Coarse particles of between 20 and 60 mesh were obtained having a density of 0.85g/cc.

Examples XII through XVI demonstrate the ability of the sweetener composition of the present invention to be dried to approximately 96 to 99% soluble solids, that is substantially completely dried. In this form, the sweetener composition of the present invention can be used as a direct replacement for conventional sweeteners such as powdered or granular sucrose, for example. The ability to concentrate the sweetener composition of the present invention to approximately 80% soluble liquids and to about 96 to 99% soluble solids is dependent upon the combination of maltodextrin and the fruit juice or fruit syrup concentrate as discussed in greater detail above.

EXAMPLE XVII

Preparation of a Densified Fruit Concentrate Sweetener Composition

The spray dried fruit concentrate sweetener composition of Example XII, having a density of 0.7g/cc, was densified by passing the product through two rolls which were maintained at a temperature of 35°C. As the fine amorphous powder pass through the pinch of the rolls, a pressed sheet was formed which was then ground and the product classified to obtain particles within the range of 20 to 40 mesh, was found to have a density of 0.9g/cc.

Example XVII demonstrates the ability to densify the sweetener composition of the invention in its dry form so that it has a bulk density substantially identical with that of a conventional sweetener, for example, sucrose.

EXAMPLE XVIII

Preparation of a Table Sweetener Product

A completely deflavorized fruit concentrate sweetener composition containing approximately 49.5% complex carbohydrates, 49.5% simple sugars, and 1% nutritional components, was dried by rotary vacuum, milled and air classified to obtain particles of 20 to 40 mesh. The granular sweetener composition was then used to sweeten coffee on a weight-for weight and volume-for-volume basis instead of granular sucrose. The coffee containing the granular fruit concentrate sweetener of this invention was then compared to coffee that had been sweetened with an equivalent amount of sucrose. The sweetening composition containing product was found to be more preferred than the sucrose containing product.

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Example XVIII further demonstrates the ability to form the sweetener composition of the present invention as a dried product suitable, for example, in direct replacement of conventional table sweetener products.

EXAMPLE XIX

Preparation of a Chocolate Confectionery Product

A completely deflavorized fruit concentrate sweetener composition was blended with chocolate liquor at a level of 55 parts sweetener to 45 parts liquor, with minor parts of lecithin and vanilla. The resulting paste was milled and refined according to standard chocolate manufacturing practices to produce a chocolate having a refined sweetness similar to that of a sucrose containing product.

EXAMPLE XX

Preparation of Instant Pre-Sweetened Tea

A partially deflavorized powdered fruit concentrate sweetener composition was blended on a dry weight basis at a level of 50 parts sweetener with 50 parts dry instant tea powder and slight amounts of natural raspberry flavor. The resulting dry blend was then agglomerated and fluid bed dried to obtain an instantly soluble pre-sweetened raspberry flavored instant tea mix. One teaspoon of the tea mix was dissolved in 250 ml of water to produce a sweet, raspberry tea flavored beverage.

EXAMPLE XXI

Preparation of Hard Candies

A pineapple concentrate sweetener composition of 80% soluble solids was cooked in a vacuum pan to 94% soluble solids. The cooked syrup was then deposited and cooled to produce a hard pineapple candy that was tack free under atmospheric conditions.

Examples XIX-XXI are illustrative of various sweetened food and beverage products which can be formed including the sweetener composition of the present invention in place of a conventional sweetener such as sucrose, corn syrup and numerous other sweeteners.

Additional food and beverage products can, of course, similarly be formed with the sweetener composition of the present invention including, for example, pastries and various sweetened prepared foods as well as a variety of instant concentrated or ready to drink beverages.

Thus, there has been described above a wide variety of sweetener compositions and corresponding processes of manufacture which are considered to be encompassed by the present invention. However, the preceding description and examples are not to be taken to define the scope of the present invention. Rather, the scope of the invention is defined only by the following appended claims.

Claims

1. A fruit concentrate sweetener composition comprising a blend of a hydrolyzed starch having a dextrose equivalent (D.E.) of up to 25 and a fruit juice or fruit syrup concentrate of at least about 40% soluble solids and about 0% insoluble solids thereby forming a liquor having a dry weight composition of 40 to 65% complex carbohydrates, 35 to 55% simple sugars from the fruit juice or fruit syrup concentrate and 0 to 5% nutritional components occurring naturally in the fruit juice or fruit syrup concentrate.

2. The fruit concentrate sweetener composition of Claim 1 wherein the hydrolyzed starch has a D.E. of 5 to 25 and the fruit juice or fruit syrup concentrate has at least 60% soluble solids.

3. The fruit concentrate sweetener composition of Claim 2 wherein the hydrolyzed starch is malt-dextrin comprising 30 to 40% soluble solids before being blended with the fruit juice or fruit syrup concentrate, the fruit juice or fruit syrup concentrate comprising 65 to 72% soluble solids.

4. The fruit concentrate sweetener composition of Claim 1 wherein the concentrate is contacted with activated carbon for a period of time selected to partially or completely deflavorize the sweetener

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composition.

5. The fruit concentrate sweetener composition of Claim 1 wherein the concentrate is dried to 78 to 80% soluble solids to form the sweetener composition suitable for replacing corn syrup and the like.

6. The fruit concentrate sweetener composition of Claim 1 wherein the concentrate is dried to 96 to 99% soluble solids to form the sweetener composition suitable for replacing powdered or granulated sucrose and like sweeteners.

7. The fruit concentrate sweetener composition of Claim 6 wherein the concentrate is compacted to have a bulk density substantially identical to the bulk density of the replaced sweetener.

8. The fruit concentrate sweetener composition of Claim 1 wherein the concentrate is diluted with water to 35 to 45% soluble solids to form a liquor suitable for spray drying and the diluted liquor is spray dried to form a product having 96 to 99% soluble solids.

9. The fruit concentrate sweetener composition of Claim 1 wherein the clear fruit juice concentrate or fruit syrup concentrate is selected from the group consisting of grapes, pears, pineapple, apples and mixtures thereof.

10. The fruit concentrate sweetener composition of Claim 1 wherein the simple sugars are derived from the fruit juice concentrate and comprise glucose, sucrose and fructose.

11. The fruit concentrate sweetener composition of Claim 1 combined with other selected ingredients to form a sweetened food product or sweetened beverage.

12. A fruit concentrate sweetener composition according to claim 1, wherein the composition has 0 to 3% of a sweetness potentiator, balance essentially water.

13. The fruit concentrate sweetener composition of Claim 12 being contacted with activated carbon for a period of time selected to partially or completely deflavorize the sweetener composition.

14. Process for forming a fruit juice sweetener according to claim 1, comprising the steps of blending a hydrolyzed starch of less than about 25 D.E. and having 30 to 40% soluble solids, with a fruit juice or fruit syrup concentrate having at least about 40% soluble solids, and thereby forming a liquor having a dry weight composition of 40 to 65% complex carbohydrates, 35 to 55% simple sugars from the fruit juice or fruit syrup concentrate and 0 to 5% nutritional components.

15. The process of Claim 14 further comprising the step of drying the liquor to 78 to 80% soluble solids to form a syrup type sweetener.

16. The process of Claim 14 further comprising the step of drying the liquor to 96 to 99% soluble solids to form a dry sweetener.

17. The process of Claim 16 wherein the liquor is diluted to 35 to 45% soluble solids and then spray dried.

18. Use of a sweetener made in accordance with the process of any of Claims 14 to 17.

Patentansprüche

1. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat, welches eine Mischung einer hydrolysierten Stärke mit einem Dextroseäquivalent (D.E.) von bis zu 25 umfaßt und ein Fruchtsaft- oder Fruchtsirupkonzentrat von wenigstens etwa 40% löslichen Feststoffen und etwa 0% unlöslichen Feststoffen, wobei eine Flüssigkeit mit einer Trockengewichtszusammensetzung von 40 bis 65% komplexen Kohlehydraten, 35 bis 55% einfacher Zucker aus dem Fruchtsaft- oder Fruchtsirupkonzentrat und 0 bis 5% Nahrungskomponenten, welche natürlich in dem Fruchtsaft- oder Fruchtsirupkonzentrat vorkommen, gebildet wird.

2. Süßmittelzusammensetzlng auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin die hydrolysierte Stärke ein D.E. von 5 bis 25 besitzt und das Fruchtsaft- oder Fruchtsirupkonzentrat wenigstens 60% löslicher Feststoffe aufweist.

3. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 2, worin die hydrolysierte Stärke Malzdextrin ist, welches 30 bis 40% löslicher Feststoffe vor dem vermischen mit dem Fruchtsaft- oder Fruchtsirupkonzentrat umfaßt, wobei das Fruchtsaft- oder Fruchtsirupkonzentrat 65 bis 72% löslicher Feststoffe umfaßt.

4. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin das Konzentrat mit Aktivkohle für einen Zeitraum in Kontakt gebracht ist, welcher ausgewählt ist, um die Süßmittelzusammensetzung teilweise oder ganz zu entaromatisieren.

5. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin das Konzentrat auf 78 bis 80% löslicher Feststoffe getrocknet ist, um eine Süßmittelzusammensetzung zu bilden, welche für den Austausch von Getreidesirup und dergleichen geeignet ist.

6. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin das Konzentrat auf 96 bis 99% löslicher Feststoffe getrocknet ist, um die Süßmittelzusammensetzung zu bilden, welche für den Austausch pulverisierter oder granulierter Sucrose und ähnlicher Süßmittel geeignet ist.

7. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 6, worin das Konzentrat verdichtet ist, um eine Schüttdichte aufzuweisen, welche im wesentlichen mit der Schüttdichte des ersetzten Süßmittels identisch ist.

8. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin das Konzentrat mit Wasser auf 35 bis 45% löslicher Feststoffe verdünnt ist, um eine für die Sprühtrocknung geeignete Flüssigkeit zu bilden, und worin die verdünnte Flüssigkeit sprühgetrocknet ist, um ein Produkt mit 96 bis 99% löslicher Feststoffe zu bilden.

9. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin das klare Fruchtsaftkonzentrat oder Fruchtsirupkonzentrat aus der Gruppe bestehend aus Trauben, Birnen, Ananas, Äpfeln und Mischungen davon ausgewählt ist.

10. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin die einfachen Zucker aus dem Fruchtsaftkonzentrat abgeleitet sind und Glucose, Sucrose und Fructose umfassen.

11. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, welches mit anderen ausgewählten Bestandteilen kombiniert ist, um ein gesüßtes Nahrungsprodukt oder ein gesüßtes Getränk zu bilden.

12. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 1, worin die Zusammensetzung 0 bis 3% eines Süßeverstärkers enthält und der Rest im wesentlichen Wasser ist.

13. Süßmittelzusammensetzung auf der Basis von Früchtekonzentrat gemäß Anspruch 12, welche mit Aktivkohle für einen Zeitraum in Kontakt gebracht wird, welcher ausgewählt ist, um die Süßmittelzusammensetzung teilweise oder ganz zu entaromatisieren.

14. Verfahren zur Herstellung eines Fruchtsaftsüßmittels gemäß Anspruch 1, welches die Schritte der Vermischung einer hydrolysierten Stärke mit weniger als etwa 25 D.E. und mit 30 bis 40% löslicher Feststoffe mit einem Fruchtsaft- oder Fruchtsirupkonzentrat mit wenigstens etwa 40% löslicher Feststoffe umfaßt, wobei eine Flüssigkeit mit einer Trockengewichtszusammensetzung von 40 bis 65% komplexer Kohlehydrate, 35 bis 55% einfacher Zucker aus dem Fruchtsaft- oder Fruchtsirupkonzentrat und 0 bis 5% Nahrungskomponenten gebildet wird.

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15. Verfahren gemäß Anspruch 14, welches des weiteren den Schritt der Trocknung der Flüssigkeit auf 78 bis 80% löslicher Feststoffe umfaßt, um ein sirupartiges Süßmittel zu bilden.

16. Verfahren gemäß Anspruch 14, welches des weiteren den Schritt der Trocknung der Flüssigkeit auf 96 bis 99% löslicher Feststoffe umfaßt, um ein trockenes süßmittel zu bilden.

17. Verfahren gemäß Anspruch 16, worin die Flüssigkeit auf 35 bis 45% löslicher Feststoffe verdünnt und dann sprühgetrocknet wird.

18. Verwendung des Süßmittels, das gemäß dem Verfahren nach einem der Ansprüche 14 bis 17 hergestellt wird.

Revendications

1. Composition d'édulcorant à base de concentré de fruits comprenant un mélange d'un amidon hydrolysé possédant un équivalent dextrose D.E. atteignant jusqu'à 25 et un concentré de jus de fruit ou un concentré de sirop de fruit contenant au moins environ 40 % de substances solides solubles et environ 0 % de substances solides insolubles, formant ainsi une liqueur possédant une composition pondérale à sec comprenant 40 à 65 % d'hydrates de carbone complexes, 35 à 55 % de sucres simples provenant du concentré de jus du fruit ou de sirop de fruits et 0 à 5 % de constituants nutritionnels apparaissant naturellement dans le jus de fruits ou dans le concentré de sirop de fruits.

2. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle l'amidon hydrolysé possède un D.E. compris entre 5 et 25 et le concentré de jus de fruits ou de sirop de fruits possède au moins 60 % de substances solides solubles.

3. Composition d'édulcorant à base de concentré de fruits selon la revendication 2, dans laquelle l'amidon hydrolysé est de la dextrine de malt comprenant 30 à 40 % de substances solides solubles avant d'être mélangé au concentré de jus de fruits ou de sirop de fruits, le concentré de jus de fruits ou de sirop de fruits comprenant 65 à 72 % de substances solides solubles.

4. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle le concentré est placé en contact avec du charbon activé pendant un intervalle de temps choisi de manière à supprimer partiellement ou complètement l'arôme de la composition d'édulcorant.

5. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle le concentré est séché pour fournir 78 à 80 % de substances solides solubles de manière à former la composition d'édulcorant convenant pour remplacer le sirop de glucose et analogue.

6. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle le concentré est séché de manière à fournir 96 à 99 % de substances solides solubles pour former la composition d'édulcorant convenant pour remplacer du sucrose à l'état de poudre ou de granulés et des édulcorants semblables.

7. Composition d'édulcorant à base de concentré de fruits selon la revendication 6, dans laquelle le concentré est tassé de manière à présenter une densité en vrac sensiblement identique à la densité en vrac de l'édulcorant remplacé.

8. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle le concentré est dilué avec de l'eau avec environ 35 à 45 % de substances solides solubles de manière à former une liqueur convenant pour un séchage par pulvérisation, et la liqueur diluée est séchée par pulvérisation de manière à former un produit possédant 96 à 99 % de substances solides solubles.

9. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle le concentré de jus de fruits clair ou le concentré de sirop de fruits est choisi dans le groupe comprenant des raisins, des poires, des ananas, des pommes et des mélanges de ces fruits.

10. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle les sucres simples sont dérivés du concentré de jus de fruits et comprennent du glucose, du sucrose et du fructose.

11. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, combiné à d'autres ingrédients choisis, pour former une denrée alimentaire sucrée ou une boisson sucrée.

12. Composition d'édulcorant à base de concentré de fruits selon la revendication 1, dans laquelle la composition possède 0 à 3 % d'un potentialisateur de douceur, le reste étant constitué essentiellement par de l'eau.

13. Composition d'édulcorant à base de concentré de fruits selon la revendication 12, placé en contact avec du charbon activé pendant un intervalle de temps sélectionné de manière à supprimer partiellement ou complètement l'arôme de la composition d'édulcorant.

14. Procédé pour former un édulcorant à base de concentré de fruits selon la revendication 1, comprenant les étapes consistant à mélanger de l'amidon hydrolysé possédant un équivalent D.E. inférieur à environ 25 et contenant 30 à 40 % de substances solides solubles, avec un concentré de jus de fruits ou de sirop de fruits possédant au moins environ 40 % de substances solides solubles, et former ainsi une liqueur possédant une composition pondérale à sec comprenant 40 à 65 % d'hydrate de carbone com plexes, 35 à 55 % de sucres simples tirés du concentré de jus du fruit ou de sirop de fruits et 0 à 5 % de constituants nutritionnels.

15. Procédé selon la revendication 14, comprenant en outre les étapes consistant à sécher la liqueur pour obtenir 78 à 80 % de substances solides solubles pour former un édulcorant du type sirop.

16. Procédé selon la revendication 14, comprenant en outre l'étape consistant à sécher la liqueur pour obtenir 96 à 99 % de substances solides pour former un édulcorant sec.

17. Procédé selon la revendication 16, selon lequel la liqueur est diluée à 35 à 45 % de substances solides solubles, puis est séchée par pulvérisation.

18. Utilisation de l'édulcorant réalisé conformément au procédé selon l'une quelconque des revendications 14 à 17.

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(54) **PROCESS AND APPARATUS FOR PRODUCING A GRANULATE BY SPRAY DRYING.**

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Description

The present invention relates to a process and an apparatus for producing a substantially dust-free granulate with a desired mean particle size and a narrow particle size distribution by spray drying.

In the present context "granulation" is defined as the building up of larger solid particles from smaller solid particles, also referred to as "(fine) solid starting material/particles"; "granulate" and "granulate material" is defined as the product obtained by granulation.

It is well known that granulate material may be produced by using fluidized bed methods where a solution or suspension of the material to be granulated is sprayed on or into a fluidized bed containing solid particles to be granulated. It is also well known that the finer part of the product discharged from the fluidized bed may be returned for further granulation in the fluidized bed, cf. DEOS 22 31 445; DEOS 25 55 917; EP 87 039 and EP 163 836.

A typical feature of the fluidized bed methods consists in that the granulation process is taking place under conditions corresponding to a completely stirred reactor. Therefore, these methods operate with long residence times for the solid particles. The solid starting material is substantially identical with the material discharged from the granulation zone, and it is thus generally necessary to separate the discharged material into three fractions, viz. a fine undersize fraction, a product fraction and an oversize fraction, which may be ground and returned to the granulation zone.

The term "granulation efficiency" is defined as the weight fraction of material leaving the granulation zone which falls within a specified, desired product range. The "recycle ratio" is defined as the weight ratio between recirculated material and material withdrawn as product.

Until now no efficient fluidized bed process has been disclosed yielding a dust-free product with desired mean particle size and a narrow particle size distribution.

It is further known that the products produced by ordinary spray drying generally have a low mean particle size, typically within the range 50-150 µm, in some cases even less and often present serious dust problems.

In order to produce larger sized particles utilizing the principles of spray drying combined spray drying, fluidized bed and agglomeration processes have been suggested.

From US PS 3,849,233 and EP 97 484 a process is known wherein a fluidized bed is arranged at the lower part of the drying chamber of a spray drying unit. In this process the particles produced in the spray drying zone are blown into the fluidized bed by the drying gas from the spray drying zone. Hereby particles from the fluidized bed are blown up into the spray drying zone. Since the spray drying zone is operated to provide exit particles with a rather high moisture content agglomeration may take place in the spray drying zone as well as in the fluidized bed.

From US PS 3,735,792 another combined spray drying fluidized bed and agglomeration process is known. This process takes also place in a chamber containing a fluidized bed arranged at the bottom of said chamber. Liquid feed is sprayed as droplets into the chamber by a fluid atomizer arranged at the top of the chamber. Primary air enters through a perforated plate at the bottom of the chamber and acts as fluidization and drying air. Secondary air fed in at the top of the chamber imparts a spiral motion to the air flow in the chamber whereby particles are withdrawn from the upper part of the fluidized bed and suspended particles are caused to make a circulatory motion in the zone above the fluidized bed. Granulates are thus formed by collision between particles and droplets and between moist particles, presumably mainly in the fluidized bed. Particles are continuously discharged from the fluidized bed, preferably via a discharge pipe countercurrently to a rising air stream, which may return a certain amount of the fines in the withdrawn product to the fluidized bed whereby a limited reduction of the dust content of the product may be achieved.

Finally, the so-called straight-through process should be mentioned as a combined spray drying and granulation process. By this process the product withdrawn from the spray drying zone is subjected to a further drying step in a fluidized bed. Particles removed from the fluidized bed by the fluidizing gas are returned to the spray drying zone and granulation takes place in this zone by collision between return particles and droplets and between moist return particles.

It is important to observe that the particle build-up mechanisms in a fluidized bed process differ from that of a spray drying granulation process. The most essential differences being the following:

As mentioned above the fluidized bed granulation process corresponds to a reaction in a completely stirred reactor having a long residence time for the reactor content, wherein the solid starting material, as defined above, is substantially identical with the material discharged from the granulation zone, whereas the process comprising granulation in the spray drying zone is similar to the reaction in a plug flow reactor with a very short residence time for the reactants, wherein the solid starting material is substantially identical with the recirculated material.

In the fluidized bed granulation process only a minor amount of liquid is introduced per second relative to

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the solid material available, whereas a much larger specific amount of liquid is introduced in the spray drying granulation process. It is desired to operate with a high liquid solid ratio in the granulation zone because this favours high strength of the granulates. However, fluidized bed granulation process cannot be safely operated at such high ratios, because the process becomes increasingly unstable, when the liquid solid ratio is increased, the problem being an increasing risk for break down of the granulation process due to formation of large lumps of sticky material.

In all granulation processes it is necessary to introduce or create fine starting particles necessary for the build-up of the granulated particles. In the fluidized bed granulation process these fine starting particles are mainly generated by attrition or grinding of already formed granulates and the rate of introduction of these fine particles into the granulation process can only be effectively controlled by controlled introduction of ground granulates, e.g. oversize particles. In contrast, fine starting particles are easily produced in the spray drying agglomeration by evaporation of droplets which have not collided with solid particles in the spray drying zone.

In the fluidized bed granulation process the starting particles are generally only comprising a small percentage of fine particles, whereas a large percentage of fine starting particles is characteristic for the known granulation processes involving spray drying. This high percentage is actually representing a problem in the straight-through process because it leads to the formation of a granulated product with an unacceptably high content of dust.

Granulates produced in a fluidized bed are in general rather coarse with a typical mean particle size about 1-5 mm, whereas granulates produced in a spray drying zone in general have a mean particle size less than about 300 μm.

For environmental reasons the demand for a low dust content in solid products has increased considerably during recent years, not least in respect of products for use in agriculture and the dyestuff industry. These demands have only with great difficulty been satisfied in respect of products produced according to the known art.

The object of the invention is to provide a process and an apparatus for producing a granulated product

- with a low dust content;
- with a desired mean particle size (d_{50});
- with d_{50} value smaller than or equal to about 1000 μm, preferably within the interval 150-400 μm;
- with a narrow particle size distribution corresponding to at least 70, preferably at least 80 % by volume, between 0.5 d_{50} and 1.5 d_{50}; and
- having high abrasion strength and excellent fluid-mechanical properties;

by a spray drying granulation process in which

- the recycle ratio is kept at a very low level;
- the mass ratio between liquid and solid feed to the spray drying and granulation zone is high;
- the formation of dust is reduced to a minimum;
- the residence time of the material in the granulation zone is kept at a very low level; and
- a subsequent cooling of the granulated product can be performed in a highly efficient way;

which method can be carried out in/which apparatus is a compact apparatus which, if desired, may be constructed by slight and inexpensive modification of existing spray drying plants.

We have now found that the object of the invention set forth above can be attained by a process for producing a substantially dust-free granulate with a desired mean particle size and a narrow particle size distribution by spray drying a solution or suspension of the material to be granulated comprising the steps of

atomizing the solution or suspension to droplets in an atomizing zone in the upper part of a spray drying and granulation zone in a drying chamber;

contacting said atomized solution or suspension with a central downward stream of drying gas and a stream of solid feed particles introduced on blown directly into the upper part of the spray drying and granulation zone to obtain a granulate by enlargement of the size of said particles by collision between droplets and feed particles and between moist feed particles;

adjusting the amount of introduced solution or suspension to the amount and drying capacity of introduced drying gas to ensure a desired moisture content of the particles or granulates leaving the spray drying and granulation zone and evaporation of non colliding droplets to formation of fine particles;

withdrawing a stream of spent drying gas from the spray drying and granulation zone;

withdrawing the particles or granulates leaving the spray drying and granulation zone from the drying chamber; and

subjecting said withdrawn particles or granulates to a size classification into two fractions in a counter-current gas/gravity classifier, preferably multistage, wherein the particles or granulates are introduced in a rising gas stream in a separation zone and separated into a coarse fraction of the predetermined particle size which is withdrawn as product and an undersize fraction, which is withdrawn from the separation zone as an entrained

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suspension in the exit gas from the classifier and returned to the spray drying and granulation zone as solid feed particles.

By this method it is possible to produce a substantially dust-free granulated product with a d_{50} value within the desired range and the desired narrow particle size distribution having high abrasion strength and excellent fluid-mechanical properties.

The granulate obtained by the method according to the invention may typically exhibit a mean particle size within the interval 150-400 µm; a particle size distribution showing at least 70, typically at least 80 % by volume particles in the interval [0.5 d_{50}, 1.5 d_{50}] and exhibit a low content of dust.

The recycle ratio is low, the mass ratio between liquid and solid feed to the spray drying and granulation zone is high and the residence time of the material in the granulation zone may be kept at a very low level, which is particularly advantageous when granulating heat sensitive materials.

One of the characteristic features of the invention resides in the fact that the use of a countercurrent gas/gravity classifier allows a very "sharp cut" as defined below:

The efficiency of a particle size classifier may be expressed by the so-called grade efficiency curve which is a graph showing g(x) as a function of x, where x is particle size and g(x) is the volume percent of particles separated as coarse particles in the size range [x,x+dx].

A classifier exhibiting a "sharp cut" is defined as a classifier with a low value for x_{90}/x_{10}, typically less than 6.0; where x_y is defined by $g(x_y) = y$. Countercurrent gas/gravity classifiers exhibiting x_{90}/x_{10}-values less than 6.0 are obtainable in practice, and x_{90}/x_{10}-values less than 4.2 and even less than 2.5 can also be achieved by these classifiers.

An essential advantage of using a countercurrent gas/gravity classifier resides in that the cut size, defined as the value of x_{50}, may be varied within a rather broad range, e.g. by adjusting the gas velocity in the classifier, typically between 0,3 and 3 m/s, independently of the other process parameters. A selected mean particle size of the granulate product is obtained by selecting a suitable value for the cut size of the classifier.

A further essential advantage of using a countercurrent gas/gravity classifier consists in the "sharp cut" obtained by using this type of classifier, which ensures an extremely favourable particle distribution of the stream of solid feed particles introduced into the upper part of the spray drying and granulation zone, which, as mentioned above, is substantially identical with the particle distribution of the solid starting material in the granulation process according to the invention.

Since only a minor amount of coarse particles are recirculated to the granulation zone not only the desired narrow particle size distribution of the product, but also the desired granulation efficiency are obtained.

Another characteristic feature of the countercurrent gas/gravity classifier resides in the possibility of operating with a relatively small gas volume compared with the gas volume used in a far less efficient fluidized bed classifier.

Since the process according to the invention operates with a high ratio between the liquid feed and fine solid starting material high granulate strength is obtained.

The solution or suspension may be atomized to droplets in a rotary atomizer, a pressure nozzle atomizer or a pneumatic or two-fluid atomizer.

The exit gas from the spray drying granulation zone may entrain fine particles from the granulation zone. If desired, these "exit gas particles" may be precipitated, e.g. in a cyclone, and returned to the spray drying granulation zone, preferably to the upper part of that zone.

The recirculated particles from the classifier and the exit gas particles if returned are preferably introduced into the spray drying granulation zone in the immediate vicinity of the atomizing zone.

The moisture content of the particles or granulates leaving the spray drying and granulation zone is preferably adjusted to a value ensuring that said particles or granulates do not exhibit any sticky character. This measure is particularly important when the process does not comprise further drying in a second drying zone in a fluidized bed.

This process is suited for agglomerating a large number of materials including
agrochemical compounds such as pesticides, e.g. insecticides, acaricides, nematodicides and fungicides, herbicides, plant growth controlling compounds and fertilizers;
pharmacologically active compounds;
animal feed products;
food products including milk products;
dyestuffs and pigments;
resins and polymers;
and other organic and inorganic substances including fermentation products, plant extracts, amino acids and proteins, enzymes, food additives, and byproducts from the slaughterhouse, dairy and paper and pulp industry.

The process is particularly suited for granulating heat sensitive materials.

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If desired, the particles or granulates leaving the spray drying and granulation zone may be subjected to further drying in a second drying zone comprising a fluidized bed arranged at the bottom of the drying chamber before they are withdrawn from the drying chamber.

If desired, further granulation may be achieved in the fluidized bed, e.g. by spraying a minor amount of liquid into or onto the fluidized bed.

According to a preferred embodiment a multistage countercurrent gas/gravity classifier is employed, preferably a "zigzag classifier". The construction and operation principles of zigzag classifiers are well known and described in e.g. GB PS 468 212.

When the process according to the invention is carried out without a second drying zone in a fluidized bed at the bottom of the drying chamber the undersize fraction from the classifier may be reintroduced via a particle exit opening at the bottom of the spray drying agglomeration chamber and blown directly into the upper part of the spray drying and granulation zone by the exit gas from the classifier.

However, improved contact between droplets and recirculated material may be achieved in an embodiment where the particles or granulates leaving the spray drying and granulation zone are withdrawn from the drying chamber via a gas lock and the undersize fraction from the classifier is transported to the upper part of the spray drying and granulation chamber entrained by the exit gas from the classifier and introduced into said upper part, optionally after having been separated from said exit gas.

When the process according to the invention is carried out with a second drying zone in a fluidized bed at the bottom of the drying chamber the particles or granulates may be withdrawn through an exit opening situated at the upper part of the fluidized bed, the undersize fraction being reintroduced via said exit opening and blown directly into the upper part of the spray drying and granulation zone by the exit gas from the classifier.

However, improved contact between droplets and recirculated material may be achieved in an embodiment wherein the particles or granulates are withdrawn from the lower part of the fluidized bed via a gas lock or through an exit opening situated at the upper part of the fluidized bed and the undersize fraction from the classifier is transported to the upper part of the spray drying and granulation chamber entrained by the exit gas from the classifier and introduced into said upper part, optionally after having been separated from said exit gas.

According to a preferred embodiment the cut size of the air classifier is selected within the interval 1.2-5.5 times the upper limit for the dust interval, defined as the size range for unacceptable fines in the product, preferably in the interval 2.0-3.5 times the said upper limit.

According to another preferred embodiment the recycle ratio is selected within the range 0.15-3, preferably within the range 0.2-1.0.

According to a further preferred embodiment the classifier is adjusted to provide a separation efficiency corresponding to a x_{90}/x_{10}-value (as defined above) less than 6.0, preferably less than 4.2, in particular less than 2.5.

According to a preferred embodiment the countercurrent gas/gravity classifier is utilized as a cooler by introducing a cold gas into the classifier.

This embodiment is particularly advantageous because of a very efficient countercurrent heat exchange, resulting in a substantial reduction of the volume of cooling gas, and a very compact apparatus, compared to the alternative: a fluidized bed cooler.

The process may be carried out in an apparatus for producing a substantially dust-free granulate with a desired mean particle size and a narrow particle size distribution by spray drying a solution or suspension of the material to be granulated comprising a spray drying granulation chamber with substantially conical, downward tapering walls provided with

a drying gas inlet, and a liquid inlet provided with an atomizer, arranged in the upper part of the chamber;
a drying gas outlet;
an inlet for a stream of solid feed particles;
a material outlet arranged at the lower part of the chamber connected to a material inlet of a countercurrent gas/gravity classifier with a separation gas inlet, a product outlet provided with a gas lock and an outlet for a fraction of fine particles suspended in separation gas connected to the inlet for the stream of solid feed particles.

According to a preferred embodiment the material outlet of the chamber is connected to the material inlet of the classifier via a gas lock, and the inlet for the stream of solid feed particles is arranged in the upper part of the chamber and connected to the fine material fraction outlet of the classifier via a conduit.

According to another preferred embodiment a perforated horizontal plate for supporting a fluidized bed and an inlet for fluidizing gas are arranged at the bottom of the chamber.

According to a further preferred embodiment an opening functioning as material outlet of the chamber as

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well as inlet for the stream of solid feed particles is arranged at the lower part of the chamber at a position over the perforated horizontal plate for supporting the fluidized bed.

According to yet a further preferred embodiment the material outlet of the chamber is arranged at the perforated horizontal plate for supporting the fluidized bed and connected to the material inlet of the classifier via a gas lock or as an opening arranged at the lower part of the chamber at a position over the perforated horizontal plate for supporting the fluidized bed and connected to the material inlet for the classifier; and the inlet for the stream of solid feed particles is arranged in the upper part of the chamber and connected to the fine material fraction outlet of the classifier via a conduit.

The invention is further described with reference to the drawing illustrating the present invention.

On the drawing

- figure 1 and 2 show schematically lay-outs for a spray drying granulation process without fluidized bed;
- figure 3 and 4 show schematically lay-outs for a spray drying granulation process comprising a fluidized bed;
- figure 5 and 6 are photomicrographs of particles of protein produced by the process according to the invention and ordinary spray drying, respectively; and
- figure 7 shows a graph of d_{50} as a function of the gas velocity, v, in the air classifier.

In fig. 1 1 represents a spray drying granulation chamber provided with a drying gas inlet 2, two drying gas outlets 3, a drying gas outlet may also be arranged at the lower part of the chamber 1, and a liquid inlet 4 provided with an atomizer. The chamber 1 has a material outlet 5 connected to a countercurrent gas/gravity classifier 6 with a gas inlet 7, an outlet 8 for fines suspended in gas and a product outlet 9 provided with a rotary valve 14.

In operation hot drying gas is introduced via the drying gas inlet 2 and liquid is introduced into the chamber 1 via a liquid inlet 4 and atomized to droplets. A part of these droplets evaporate under formation of fine solid particles and a substantial part of these droplets collide with the fine particles recirculated from the classifier 6 under formation of granulates which are withdrawn with the fine solid particles from the granulation chamber via the material outlet 5 and screened in the air classifier 6. The granulated end product is discharged as the coarse fraction from the classifier 6 via the product outlet 9. The spent drying gas from the spray drying granulation zone is withdrawn via the gas outlets 3. This gas may contain entrained fine particles which, if desired, may be precipitated in a cyclone or a filter and returned to the spray drying granulation zone.

In fig. 2 1 represents a spray drying granulation chamber and 2, 3, 4, 6, 7, 8, 9 and 14 refer to corresponding apparatus parts as above. In this embodiment the outlet 8 is connected to a transfer pipe 10 with an opening 11 situated in the immediate vicinity of the atomizing zone. The recirculated fine material may be precipitated in a not shown cyclone before it is introduced into the spray drying granulation zone. In this case the material outlet 5 is provided with a rotary valve 15.

In fig. 3 1 represents a spray drying granulation chamber provided with a fluidized bed 12 having a fluidization gas inlet 13 and arranged at the bottom of the chamber 1. Reference numerals 2, 3, 4, 5, 6, 7, 8, 9 and 14 refer to corresponding apparatus parts as above. But in this case the material outlets 5 and 8 are arranged at the upper part of the surface of the fluidized bed 12.

In operation heating gas is introduced via the heating gas inlet 2 and liquid is introduced into the chamber via the liquid inlet 4 and atomized to droplets. A part of these droplets evaporate under formation of fine solid particles and a substantial part of these droplets collide with the fine particles recirculated from the classifier 6 under formation of granulates. These granulates and the fine solid particles are transferred to the fluidized bed 12 where they are subjected to further drying. The material is withdrawn from the fluidized bed via the material outlet 5 and screened in the air classifier 6. The granulated end product is discharged as the coarse fraction from the classifier 6 via the product outlet 9. The spent heating gas from the spray drying granulation zone is withdrawn via the gas outlets 3. This gas may contain entrained fine particles which, if desired, may be precipitated in a cyclone and returned to the spray drying granulation zone.

In fig. 4 1 represents a spray drying granulation chamber provided with a fluidized bed 12 having a fluidization gas inlet 13 and arranged at the bottom of the chamber 1. Reference numerals 2, 3, 4, 5, 6, 7, 8, 9 and 14 refer to corresponding apparatus parts as above. But in this case the material outlet 5 is arranged at the bottom of the fluidized bed 12 and provided with a rotary valve 15, and the outlet 8 is connected to a transfer pipe 10 with an opening 11 situated in the immediate vicinity of the atomizing zone. Also in this case the recirculated fine material may be precipitated in a not shown cyclone before it is introduced into the spray drying granulation zone.

These embodiments are only given as examples. In another preferred embodiment the material outlet 5 is arranged as shown in fig. 3, whereas the outlet 8 of the classifier 6 is connected to a transfer pipe 10 with an opening 11 situated in the immediate vicinity of the atomizing zone as shown in fig. 4.

The process according to the invention will be further illustrated by means of the following examples.

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EXAMPLE 1

A suspension of single-cell protein with a content of 13% dry matter was granulated in an apparatus according to the invention by means of a rotary atomizer. In this apparatus the material outlet 5 was arranged as shown in fig. 3, the outlet 8 of the classifier 6 was connected to a transfer pipe 10 with an opening 11 situated in the immediate vicinity of the atomizing zone as shown in fig. 4, and the gas outlet 3 was arranged not at the upper part of the chamber, but at the lower part over the surface of the internal fluidized bed.

The amount of feed was approx 800 kg/h. The granulated material was via an internal fluidized bed in the chamber passed to a countercurrent gas/gravity classifier. The internal fluidized bed was used for afterdrying and distribution of the granulate to the classifier. The amount of drying air introduced into the spray drying chamber was approx. 7000 kg/h, and the amount of air for the classifier which was also used as a cooler (cold separation air) was 160 kg/h corresponding to a gas velocity in the classifier of 0.5 m/s. Fine particles from the air classifier as well as fine particles separated from the exit gas from the spray drying granulation chamber were recirculated to the atomizing zone by means of a pneumatic conveyor system.

Further process conditions and data are shown in table 1.

TABLE 1

Temperature	
Feed, °C	40
Inlet gas to chamber, °C	338
Gas to classifier, °C	21
In fluidized bed, °C	63
Exit gas from chamber, °C	87
RH*) in chamber, %	25
MC*) in product, %	4.1
Classifier properties	
x_{90}/x_{10} ratio	about 4
Cut size/upper dust limit ratio	about 2.6

*) RH: Relative humidity; MC: Moisture content

The granulates withdrawn as product from the air classifier had a temperature of 28°C and exhibited a particle size distribution, which can be expressed as a Rosin-Rammler-distribution having a mean size of 157 µm and a slope of 3.2, corresponding to d_{50} = 140 µm, and 73% by vol. between 0.5 d_{50} and 1.5 d_{50}.

A scanning picture of these granulates is shown in fig. 5.

For reasons of comparison a suspension of the same starting material but with a content of 25% dry matter was spray dried in a corresponding ordinary spray dryer. Fig. 6 shows a scanning picture of the single-cell particles obtained as a product by this process. This product exhibited: d_{50}: 20 µm, and 66 % vol. between 0.5 d_{50} and 1.5 d_{50}.

The flowability-properties of these products were determined by measurement of the Hausner ratio.

As further described in e.g. Svarovsky, L., Powder Testing Guide, Elsevier (1987) the Hausner ratio is defined as the ratio of the tapped bulk density to the untapped bulk density.

A value of the Hausner ratio close to unity indicates weak interparticle forces ensuring excellent flowability, whereas a high value e.g. greater than 1.4 indicates poor flowability.

The Hausner ratio for the product produced according to the invention was measured to 1.06, and the Hausner ratio for the product produced by ordinary spray drying was measured to 1.46.

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EXAMPLE 2

An aqueous suspension of an organic agricultural chemical with a content of 32% dry matter was granulated in an apparatus similar to the one used in example 1. However, the suspension was not atomized by means of a rotary atomizer, but by a nozzle with a working pressure of 70 bar, and the gas outlet was arranged in the upper part of the chamber as shown in fig. 3. A minor amount of the suspension was sprayed directly onto the internal fluidized bed by a secondary nozzle arranged immediately over the internal fluidized bed. Approx. 350 kg aqueous suspension were atomized per hour, 15% thereof through the secondary nozzle. The classifier was operated with an amount of air of 530 kg/h corresponding to a gas velocity of 1.5 m/s in the classifier.

Further process conditions and data are shown in table 2.

TABLE 2

Temperature	
Feed, °C	34
Inlet gas to chamber, °C	198
Gas to classifier, °C	21
In fluidized bed, °C	72
Exit gas from chamber, °C	87
RH*) in chamber, %	10
MC*) in product, %	6.5
Classifier properties	
x_{90}/x_{10} ratio	about 3
Cut size/upper dust limit ratio	about 2.6

*) RH: Relative humidity; MC: Moisture content

The resulting product was non-dusting and contained only 2% by volume particles of a size less than 125 µm. The particle size distribution was characterized by: d_{50}= 495 µm, and 88% between 0.5 d_{50} and 1.5 d_{50}.

The flowability-properties of this product was determined by measurement of Hausner ratio: The Hausner ratio for the product produced according to the invention was measured to 1.11.

EXAMPLE 3

Sulfite liquor from a plant for treating cellulose by the sulfite process having a content of dry matter of approx. 50% was granulated in an apparatus similar to the one used in example 1. Between 600 and 700 kg of this liquor was atomized per hour.

Further process conditions and data are shown in table 3.

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TABLE 3

Temperature	
Feed, °C	approx. 40
Inlet gas to chamber, °C	220
Gas to classifier, °C	23-26
In fluidized bed, °C	70
Exit gas from chamber, °C	94
RH*) in chamber, %	10
MC*) in product, %	4

*) RH: Relative humidity; MC: Moisture content

Three series of tests were carried out in which the classifier was operated at three different air velocities while the other process conditions were kept essentially constant. For each value of the air velocity the particle distribution in the resulting product was determined. The results showed that the particle size increased monotonously with increasing air velocity in the classifier. The amount of small particles was also reduced when the air velocity was increased.

The results are shown in the following table 4 and in fig. 7:

TABLE 4

Air velocity m/s	Median diameter d_{50} µm	Amount less than 50 µm %
0.6	110	12
1.1	140	7
1.6	171	5

The flowability-properties of these products were determined by measurement of the Hausner ratio:

The Hausner ratios for the products produced according to the invention were measured to 1.22, and did not show any significant variation as function of the air velocity in the classifier.

EXAMPLE 4

Sulfate liquor from a plant for treating cellulose by the sulfate process having a content of dry matter of approx. 30% was granulated in an apparatus similar to the one used in example 1. Spray drying of sulfate liquor normally results in a product containing large amounts of dust.

Two tests were carried out. In the first test a rotary atomizer was used. In the second the feed was atomized by means of a nozzle having a working pressure of 80 bar.

In both tests approx. 400 kg of this liquor was atomized per hour.

Further process conditions and data are shown in table 5.

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TABLE 5

	(rot.a./nozzle)
Temperature	
Feed, °C	approx. 60
Inlet gas to chamber, °C	170/175
Gas to classifier, °C	26
In fluidized bed, °C	66
Exit gas from chamber, °C	72/75
RH*) in chamber, %	19/17
MC*) in product, %	4
Classifier properties	
x_{90}/x_{10} ratio	about 3

*) RH: Relative humidity; MC: Moisture content

The air velocity in the classifier was 1.5 m/s corresponding to an amount of air of 520 kg/h.

Particle size distribution and flowability data for the products are shown in table 6. For reasons of comparison corresponding data for a product produced by ordinary spray drying are also shown in table 6.

TABLE 6

	Median diameter d_{50} µm	Amount less than 50 µm %	Hausner ratio
Test with rotary atomizer, I*)	144	3	1.21
Test with nozzle, I*)	160	2	1.19
Test with ordinary spray drying, C*)	32	76	1.36

*) I: According to the invention; C: Comparison (known art)

It appears from the table that the products produced by the method according to the present invention exhibit a considerably larger particle diameter, a lower content of dust and a lower Hausner ratio than the product produced according the known art. Moreover, there is only a minor difference between the product obtained by the use of a rotary atomizer and the product obtained by the use of a nozzle atomizer.

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Claims

1. A process for producing a substantially dust-free granulate with a desired mean particle size and a narrow particle size distribution by spray drying a solution or suspension of the material to be granulated comprising the steps of
atomizing the solution or suspension to droplets in an atomizing zone in the upper part of a spray drying and granulation zone in a drying chamber;
contacting said atomized solution or suspension with a central downward stream of drying gas and a stream of solid feed particles introduced or blown directly into the upper part of the spray drying and granulation zone to obtain a granulate by enlargement of the size of said particles by collision between droplets and feed particles and between moist feed particles;
adjusting the amount of introduced solution or suspension to the amount and drying capacity of introduced drying gas to ensure a desired moisture content of the particles or granulates leaving the spray drying and granulation zone and evaporation of non colliding droplets to formation of fine particles;
withdrawing a stream of spent drying gas from the spray drying and granulation zone;
withdrawing the particles or granulates leaving the spray drying and granulation zone from the drying chamber; and
subjecting said withdrawn particles or granulates to a size classification into two fractions in a countercurrent gas/gravity classifier, preferably multistage, wherein the particles or granulates are introduced in a rising gas stream in a separation zone and separated into a coarse fraction of the predetermined particle size which is withdrawn as product and an undersize fraction, which is withdrawn from the separation zone as an entrained suspension in the exit gas from the classifier and returned to the spray drying and granulation zone as solid feed particles.

2. A process according to claim 1, wherein the particles or granulates leaving the spray drying and granulation zone are subjected to further drying in a second drying zone comprising a fluidized bed arranged at the bottom of the drying chamber before they are withdrawn from the drying chamber.

3. A process according to claim 1 or 2, wherein the countercurrent gas/gravity classifier is a multistage zigzag classifier.

4. A process according to claims 1 or 3, wherein the undersize fraction is reintroduced via a particle exit opening at the bottom of the spray drying agglomeration chamber and blown directly into the upper part of the spray drying and granulation zone by the exit gas from the classifier.

5. A process according to claims 1 or 3, wherein the particles or granulates leaving the spray drying and granulation zone are withdrawn from the drying chamber via a gas lock and the undersize fraction from the classifier is transported to the upper part of the spray drying and granulation chamber entrained by the exit gas from the classifier and introduced into said upper part, optionally after having been separated from said exit gas.

6. A process according to claims 2-3, wherein the particles or granulates are withdrawn through an exit opening situated at the the upper part of the fluidized bed and the undersize fraction is reintroduced via said exit opening and blown directly into the upper part of the spray drying and granulation zone by the exit gas from the classifier.

7. A process according to claims 2-3, wherein the particles or granulates are withdrawn from the fluidized bed via a gas lock or through an exit opening situated at the upper part of the fluidized bed, and the undersize fraction from the classifier is transported to the upper part of the spray drying and granulation chamber entrained by the exit gas from the classifier and introduced into said upper part, optionally after having been separated from said exit gas.

8. A process according to claims 1-7, wherein the cut size of the air classifier is selected within the interval 1.2-5.5 times the upper limit for the dust interval, defined as the size range for unacceptable fines in the product, preferably in the interval 2.0-3.5 times the said upper limit.

9. A process according to claims 1-8, wherein the recycle ratio, defined as the weight ratio between recirculated material and withdrawn product is selected within the range 0.15-3, preferably within the range 0.2-1.0.

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10. A process according to claims 1-9, wherein the classifier is selected to provide a separation efficiency corresponding to a x_{90}/x_{10}-value less than 6.0, preferably less than 4.2, in particular less than 2.5, where x_y is the particle size for which $g(x_y) = y$ % by volume, where g() is the graph of the grade efficiency curve of the classifier.

11. A process according to claims 1-10, wherein the product is subjected to cooling in the classifier by introducing a cold gas in the classifier.

12. An apparatus for producing a substantially dust-free granulate with a desired mean particle size and a narrow particle size distribution by spray drying a solution or suspension of the material to be granulated comprising a spray drying granulation chamber (1) with substantially conical, downward tapering walls provided with
a drying gas inlet (2), and a liquid inlet (4) provided with an atomizer, arranged in the upper part of the chamber (1);
a drying gas outlet (3);
an inlet for a stream of solid feed particles (8, 11);
a material outlet (5) arranged at the lower part of the chamber (1) connected to a material inlet of a countercurrent gas/gravity classifier (6) with a separation gas inlet (7), a product outlet (9) provided with a gas lock (14) and an outlet (8) for a fraction of fine particles suspended in separation gas connected to the inlet (8, 11) for the stream of solid feed particles.

13. An apparatus according to claim 12, wherein the material outlet (5) of the chamber (1) is connected to the material inlet of the classifier (6) via a gas lock (15), and the inlet (11) for the stream of solid feed particles is arranged in the upper part of the chamber (1) and connected to the fine material fraction outlet (8) of the classifier (6) via a conduit (10).

14. An apparatus according to claim 12, wherein a perforated horizontal plate for supporting a fluidized bed and an inlet for fluidizing gas (13) are arranged at the bottom of the chamber (1).

15. An apparatus according to claim 14, wherein an opening functioning as material outlet (5) of the chamber (1) and inlet (8) for the stream of solid feed particles is arranged at the lower part of the chamber (1) at a position over the perforated horizontal plate for supporting the fluidized bed.

16. An apparatus according to claim 14, wherein the material outlet (5) of the chamber (1) is arranged at the perforated horizontal plate for supporting the fluidized bed and connected to the material inlet of the classifier (6) via a gas lock (15) or as an opening arranged at the lower part of the chamber (1) at a position over the perforated horizontal plate for supporting the fluidized bed and connected to the material inlet for the classifier (6); and the inlet (11) for the stream of solid feed particles is arranged in the upper part of the chamber (1) and connected to the fine material fraction outlet (8) of the classifier (6) via a conduit (10).

Patentansprüche

1. Verfahren zur Herstellung eines im wesentlichen staubfreien Granulates mit einer gewünschten mittleren Partikelgröße und einer engen Partikelgrößenverteilung durch Sprühtrocknen einer Lösung oder Suspension des zu granulierenden Materials, das die folgenden Schritte aufweist
Zerstäuben der Lösung oder Suspension zu Tröpfchen in einer Zerstäubungszone im oberen Teil einer Sprühtrocknungs- und Granulationszone in einer Trocknungskammer,
in Kontakt Bringen der zerstäubten Lösung oder Suspension mit einem zentralen abwärtsgerichteten Trocknungsgas-Strom und einem Strom aus festen Einspeisungspartikeln, die in den oberen Teil der Sprühtrocknungs- und Granulationszone zugeführt oder direkt eingeblasen werden, um ein Granulat durch Vergrößerung der Abmessung der genannten Partikel durch Kollision zwischen Tröpfchen und Einspeisungspartikeln und zwischen feuchten Einspeisungspartikeln zu erhalten,
Einstellen der Menge an zugeführter Lösung oder Suspension auf die Menge und Trocknungskapazität von zugeführtem Trocknungsgas, um einen gewünschten Feuchtigkeitsgehalt der Partikel oder Granulate, die die Sprühtrocknungs- und Granulationszone verlassen, und die Verdampfung von nichtkollidierenden Tröpfchen zur Bildung von feinen Partikeln sicherzustellen,
Abziehen eines Stromes von verbrauchtem Trocknungsgas aus der Sprühtrocknungs- und Granulations-

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zone,
Abziehen der Partikel oder Granulate, die die Sprühtrocknungs- und Granulationszone verlassen, aus der Trocknungskammer und
Größenklassifikation der abgezogenen Partikel oder Granulate in zwei Fraktionen in einem vorzugsweise mehrstufigen Gegenstromgas/Schwerkraft-Klassifizierer, wobei die Partikel oder Granulate in einen aufsteigenden Gasstrom in einer Trennzone eingeführt und in eine Grobfraktion mit der vorgegebenen Partikelgröße, die als Produkt abgezogen wird, und eine Untergrößen-Fraktion aufgeteilt werden, die aus der Trennzone als eine in dem aus dem Klassifizierer austretenden Gas mitgeführte Suspension abgezogen und als feste Einspeisungspartikel zu der Sprühtrocknungs- und Granulationszone zurückgeführt wird.

2. Verfahren nach Anspruch 1, bei dem die Partikel oder Granulate, die die Sprühtrocknungs- und Granulationszone verlassen, einer weiteren Trocknung in zweiten Trocknungszone, die ein am Boden der Trocknungskammer angeordnetes Fließbett aufweist, unterzogen werden, bevor sie aus der Trocknungskammer abgezogen werden.

3. Verfahren nach Anspruch 1 oder 2, bei dem der Gegenstromgas/Schwerkraft-Klassifizierer ein mehrstufiger Zickzack-Klassifizierer ist.

4. Verfahren nach Anspruch 1 oder 3, bei dem die Untergrößen-Fraktion über einen Partikelauslaß, der am Boden der Sprühtrocknungs-Agglomerationskammer mündet, zurückgeführt und durch das Austrittsgas aus dem Klassifizierer direkt in den oberen Teil der Sprühtrocknungs- und Granulationszone eingeblasen wird.

5. Verfahren nach Anspruch 1 oder 3, bei dem die Partikel oder Granulate, die die Sprühtrocknungs- und Granulationszone verlassen, über eine Gasschleuse aus der Trocknungskammer abgezogen werden und die Untergrößen-Fraktion aus dem Klassifizierer, mitgenommen durch das Austrittsgas aus dem Klassifizierer, zu dem oberen Teil der Sprühtrocknungsund Granulationskammer transportiert und in diesen oberen Teil zugeführt wird, wahlweise nachdem sie von dem Austrittsgas getrennt worden ist.

6. Verfahren nach Ansprüchen 2-3, bei dem die Partikel oder Granulate durch eine Austrittsöffnung abgezogen werden, die sich am oberen Teil des Fließbettes befindet, und die Untergrößen-Fraktion über diese Austrittsöffnung zurückgeführt und durch das Austrittsgas aus dem Klassifizierer direkt in den oberen Teil der Sprühtrocknungs- und Granulationszone eingeblasen wird.

7. Verfahren nach Ansprüchen 2-3, bei dem die Partikel oder Granulate aus dem unteren Teil des Fließbettes über eine Gasschleuse abgezogen werden oder durch eine Austrittsöffnung, die sich am oberen Teil des Fließbettes befindet, und die Untergrößen-Fraktion aus dem Klassifizierer, mitgenommen durch das Austrittsgas aus dem Klassifizierer, zu dem oberen Teil der Sprühtrocknungs- und Granulationskammer transportiert und in diesen oberen Teil zugeführt wird, wahlweise nachdem sie von dem Austrittsgas getrennt worden ist.

8. Verfahren nach Ansprüchen 1-7, bei dem die Trenngröße des Luft-Klassifizierers in dem Intervall gewählt wird, das dem 1,2-5,5-fachen der oberen Grenze für das Staub-Intervall entspricht, das als Größenbereich für unakzeptierbare Feinanteile in dem Produkt definiert ist, vorzugsweise in dem Intervall entsprechend dem 2,0-3,5-fachen dieser oberen Grenze.

9. Verfahren nach Ansprüchen 1-8, bei dem das Rückführungsverhältnis, das als das Gewichtsverhältnis zwischen dem zurückgeführten Mateial und dem abgzogenen Produkt definiert ist, in dem Bereich von 0,15-3, vorzugsweise im Bereich von 0,2-1,0 gewählt wird.

10. Verfahren nach Ansprüchen 1-9, bei dem der Klassifizierer so gewählt wird, daß er eine Trenneffizienz entsprechend einem x_{90}/x_{10}-Wert von weniger als 6,0, vorzugsweise weniger als 4,2, insbesondere weniger als 2,5 aufweist, wobei x_y die Partikelgröße ist, für die g(x) = y % nach Volumen ist, wobei g() der Graph der Siebkurve des Klassifizierers ist.

11. Verfahren nach Ansprüchen 1-10, bei dem das Produkt in dem Klassifizierer gekühlt wird, indem ein kaltes Gas in den Klassifizier zugeführt wird.

12. Vorrichtung zur Herstellung eines im wesentlichen staubfreien Granulates mit einer gewünschten mittleren

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Partikelgröße und einer engen Partikelgrößenverteilung durch Sprühtrocknen einer Lösung oder Suspension des zu granulierenden Materials, mit einer Sprühtrocknungs-Granulationskammer (1), mit im wesentlichen konischen, sich nach unten verjüngenden Wänden, die versehen ist
mit einem Trocknungsgas-Einlaß (2) und einem mit einem Zerstäuber versehenen Flüssigkeits-Einlaß (4), die im oberen Teil der Kammer (1) angeordnet sind,
einem Trocknungsgas-Auslaß (3),
einem Einlaß (8, 11) für einen Strom fester Einspeisungspartikel,
einem Material-Auslaß (5), der am unteren Teil der Kammer (1) angeordnet ist und verbunden ist mit einem Material-Einlaß eines Gegenstromgas/Schwerkraft-Klassifizierers (6) mit einem Trenngas-Einlaß (7), einem mit einer Gasschleuse (14) versehenen Produkt-Auslaß (9) und einem Auslaß (8) für eine Fraktion aus in dem Trenngas suspendierten feinen Partikeln, der mit dem Einlaß (8, 11) für den Strom aus festen Einspeisungspartikeln verbunden ist.

13. Vorrichtung nach Anspruch 12, bei der der Material-Auslaß (5) der Kammer (1) mit dem Material-Einlaß des Klassifizierers (6) über eine Gasschleuse (15) verbunden ist, und der Einlaß (11) für den Strom aus festen Einspeisungspartikeln im oberen Teil der Kammer (1) angeordnet und über eine Leitung (10) mit dem Auslaß (8) des Klassifizierers (6) für die Feinmaterial-Fraktion verbunden ist.

14. Vorrichtung nach Anspruch 12, bei der eine perforierte waagerechte Platte zum Tragen eines Fließbettes und ein Einlaß (13) für Fluidisierungsgas am Boden der Kammer (1) angeordnet sind.

15. Vorrichtung nach Anspruch 14, bei der eine Öffnung, die als Material-Auslaß (5) der Kammer sowie als Einlaß (8) für den Strom aus festen Einspeisungspartikeln dient, am unteren Teil der Kammer (1) in einer Position über der perforierten waagerechten Platte zum Tragen des Fließbettes angeordnet ist.

16. Vorrichtung nach Anspruch 14, bei der der Material-Auslaß (5) der Kammer (1) an der perforierten waagerechten Platte zum Tragen des Fließbettes angeordnet und mit dem Material-Einlaß des Klassifizierers (6) über eine Gasschleuse (15) verbunden oder als eine Öffnung ausgebildet ist, die am unteren Teil der Kammer (1) in einer Position über der perforierten waagerechten Platte zum Tragen des Fließbettes angeordnet und mit dem Material-Einlaß für den Klassifizierer (6) verbunden ist und der Einlaß (11) für den Strom aus festen Einspeisungspartikeln im oberen Teil der Kammer (1) angeordnet und über eine Leitung (10) mit dem Auslaß (8) des Klassifizierers (6) für die Feinmaterial-Fraktion verbunden ist.

Revendications

1. Procédé de production d'un granulé sensiblement sans poussière avec une taille de particule moyenne souhaitée et une distribution granulométrique étroite par séchage par pulvérisation d'une solution ou suspension du matériau à granuler comprenant les étapes consistant à

atomiser la solution ou suspension en gouttelettes dans une zone d'atomisation située dans la partie supérieure d'une zone de granulation et de séchage par pulvérisation dans une chambre de séchage ;

mettre en contact ladite solution ou suspension atomisée avec un flux central descendant de gaz de séchage et un flux de particules d'amenée solides introduit ou insufflé directement dans la partie supérieure de la zone de granulation et de séchage par pulvérisation pour obtenir un granulé par agrandissement de la taille desdites particules par collision entre gouttelettes et particules d'amenée et entre particules d'amenée humides ;

ajuster la quantité de solution ou de suspension introduite à la quantité et à la capacité de séchage du gaz de séchage introduit, pour assurer une teneur en eau souhaitée des particules ou granulés quittant la zone de granulation et de séchage par pulvérisation et l'évaporation de gouttelettes n'entrant pas en collision pour la formation de particules fines ;

extraire un flux de gaz de séchage épuisé de la zone de granulation et de séchage par pulvérisation ;

extraire les particules ou granulés quittant la zone de granulation et de séchage par pulvérisation provenant de la chambre de séchage ; et

soumettre lesdits granulés ou particules extraits à une classification par taille en deux fractions dans un classificateur gravimétrique/gaz à contre-courant, préférentiellement multi-étagé, dans lequel les particules ou granulés sont introduits dans un flux gazeux montant situé dans une zone de séparation et séparés en une fraction grossière de la taille de particule prédéterminée, qui est extraite en tant que bon

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produit et en une fraction de refus inférieur, qui est retirée de la zone de séparation, en tant que suspension entraînée dans le gaz de sortie provenant du classificateur, et ramenée à la zone de granulation et de séchage par pulvérisation en tant que particules d'amenée solides.

2. Procédé conforme à la revendication 1, dans lequel les particules ou granulés quittant la zone de granulation et de séchage par pulvérisation sont soumis à un séchage additionnel dans une seconde zone de séchage comprenant un lit fluidisé disposé à la base de la chambre de séchage avant d'être retirés de la chambre de séchage.

3. Procédé selon la revendication 1 ou 2, dans lequel le classificateur gravimétrique/gaz à contre-courant est un classificateur zigzag multi-étagé.

4. Procédé selon les revendications 1 ou 3, dans lequel la fraction de refus inférieur est réintroduite via une ouverture de sortie de particules à la base de la chambre d'agglomération et de séchage par pulvérisation et insufflée directement dans la partie supérieure de la zone de granulation et de séchage par pulvérisation par le gaz de sortie provenant du classificateur.

5. Procédé selon les revendications 1 ou 3, dans lequel les particules ou granulés quittant la zone de granulation et de séchage par pulvérisation sont extraits de la chambre de séchage via un sas à gaz et la fraction de refus inférieur provenant du classificateur est transportée à la partie supérieure de la chambre de granulation et de séchage par pulvérisation, est entraînée par le gaz de sortie provenant du classificateur et introduite dans ladite partie supérieure, facultativement après avoir été séparée dudit gaz de sortie.

6. Procédé selon les revendications 2-3, dans lequel les particules ou granulés sont extraits par une ouverture de sortie située à la partie supérieure du lit fluidisé, la fraction de refus inférieur est réintroduite via ladite ouverture de sortie et insufflée directement dans la partie supérieure de la zone de granulation et de séchage par pulvérisation par le gaz de sortie provenant du classificateur.

7. Procédé selon les revendications 2-3, dans lequel les particules ou granulés sont extraits du lit fluidisé via un sas à gaz ou en passant à travers une ouverture de sortie située à la partie supérieure du lit fluidisé, et la fraction de refus inférieur provenant du classificateur est transportée à la partie supérieure de la chambre de granulation et de séchage par pulvérisation, entraînée par le gaz de sortie provenant du classificateur et introduite dans ladite partie supérieure, facultativement après avoir été séparée dudit gaz de sortie.

8. Procédé selon les revendications 1-7, dans lequel la taille de fractionnement du classificateur à air est sélectionnée dans la plage comprise entre 1,2 et 5,5 fois la limite supérieure de la plage d'impuretés définie comme étant la plage de taille des fines inacceptables dans le produit, préférentiellement dans la plage allant de 2,0 à 3,5 fois ladite limite supérieure.

9. Procédé selon les revendications 1-8, dans lequel le taux de recyclage, défini comme étant le rapport pondéral entre le matériau recirculé et le produit extrait, est sélectionné dans la plage allant de 0,15 à 3, préférentiellement dans la plage allant de 0,2 à 1,0.

10. Procédé selon les revendications 1-9, dans lequel le classificateur est ajusté pour fournir un rendement de séparation correspondant à une valeur x_{90}/x_{10} inférieure à 6,0, préférentiellement inférieure à 4,2, notamment inférieure à 2,5, où x_y est la taille de la particule pour laquelle $g(x_y) = y$ % en volume, où g() est le graphe de la courbe de rendement du classificateur.

11. Procédé selon les revendications 1-10, dans lequel le produit est soumis au refroidissement dans le classificateur en introduisant un gaz froid dans le classificateur.

12. Appareil de production d'un granulé sensiblement sans poussière, avec une taille de particule moyenne souhaitée et une distribution granulométrique étroite par séchage par pulvérisation d'une solution ou suspension de matériau à granuler comprenant une chambre de granulation par séchage par pulvérisation (1) avec des parois sensiblement coniques, effilées vers le bas, avec

une entrée de gaz de séchage (2), et une entrée de liquide (4) munie d'un atomiseur, agencées dans la partie supérieure de la chambre (1) ;

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une sortie de gaz de séchage (3) ;
une entrée pour un flux de particules d'amenée solides (8, 11) ;
une sortie de matériau (5) agencée à la partie inférieure de la chambre (1), reliée à une entrée de matériau d'un classificateur gravimétrique/gaz à contre-courant (6) avec une entrée de gaz de séparation (7), une sortie de produit (9) munie d'un sas à gaz (14) et d'une sortie (8), prévue pour une fraction de particules fines en suspension dans le gaz de séparation, reliée à l'entrée (8, 11) prévue pour le flux des particules d'amenée solides.

13. Appareil selon la revendication 12, dans lequel la sortie de matériau (5) de la chambre (1) est reliée à l'entrée de matériau du classificateur (6) par l'intermédiaire d'un sas à gaz (15), et l'entrée (11) prévue pour l'écoulement des particules d'amenée solides est agencée dans la partie supérieure de la chambre (1), et est reliée à la sortie (8) de la fraction de matériau fin du classificateur (6) par l'intermédiaire d'un conduit (10).

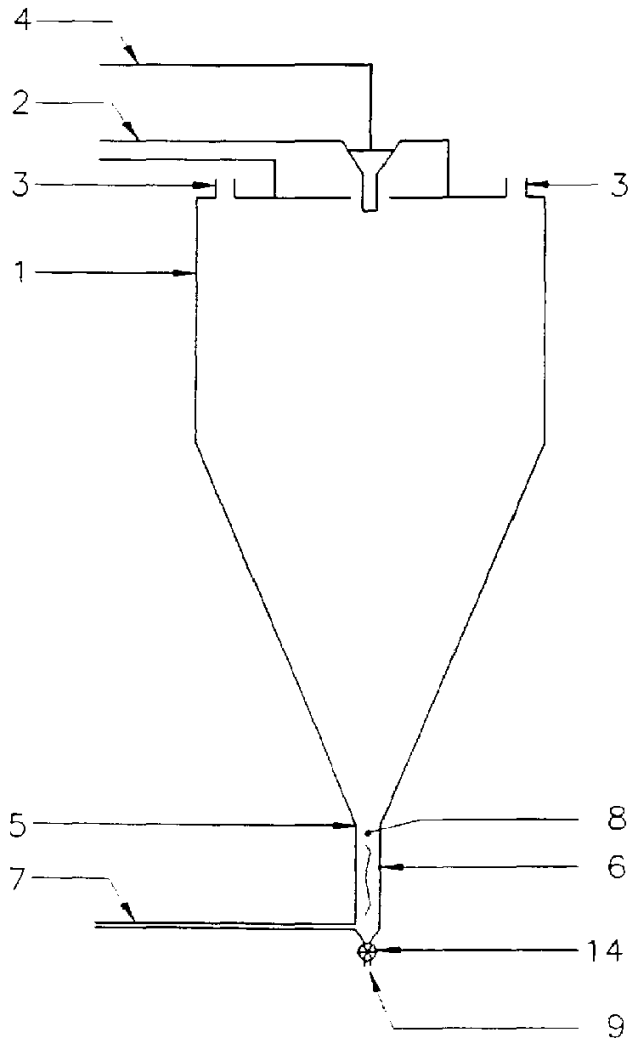
14. Appareil selon la revendication 12, dans lequel une tôle horizontale perforée pour supporter un lit fluidisé et une entrée pour le gaz fluidisant (13) sont agencées à la base de la chambre (1).

15. Appareil selon la revendication 14, dans lequel une ouverture servant de sortie de matériau (5) de la chambre (1) tout comme d'entrée (8) pour le flux des particules d'amenée solides est agencée à la partie inférieure de la chambre (1), au-dessus de la tôle horizontale perforée destinée à supporter le lit fluidisé.

16. Appareil selon la revendication 14, dans lequel la sortie de matériau (5) de la chambre (1) est agencée au niveau de la tôle horizontale perforée, destinée à supporter le lit fluidisé, et est reliée à l'entrée de matériau du classificateur (6) par l'intermédiaire d'un sas à gaz (15) ou en ouverture agencée à la partie inférieure de la chambre (1), au-dessus de la tôle horizontale perforée destinée à supporter le lit fluidisé, et reliée à l'entrée de matériau pour le classificateur (6) ; et l'entrée (11) pour le flux des particules d'amenée solides est agencée dans la partie supérieure de la chambre (1) et est reliée à la sortie (8) de la fraction de matériau fin du classificateur (6) par l'intermédiaire d'un conduit (10).

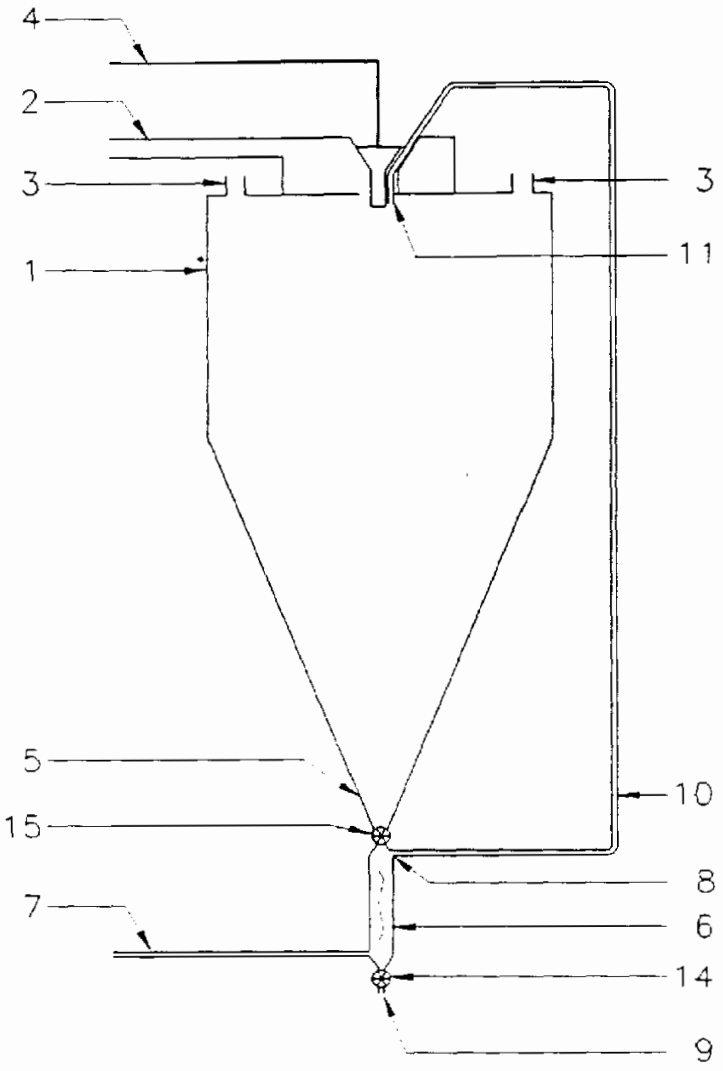
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Fig. 1



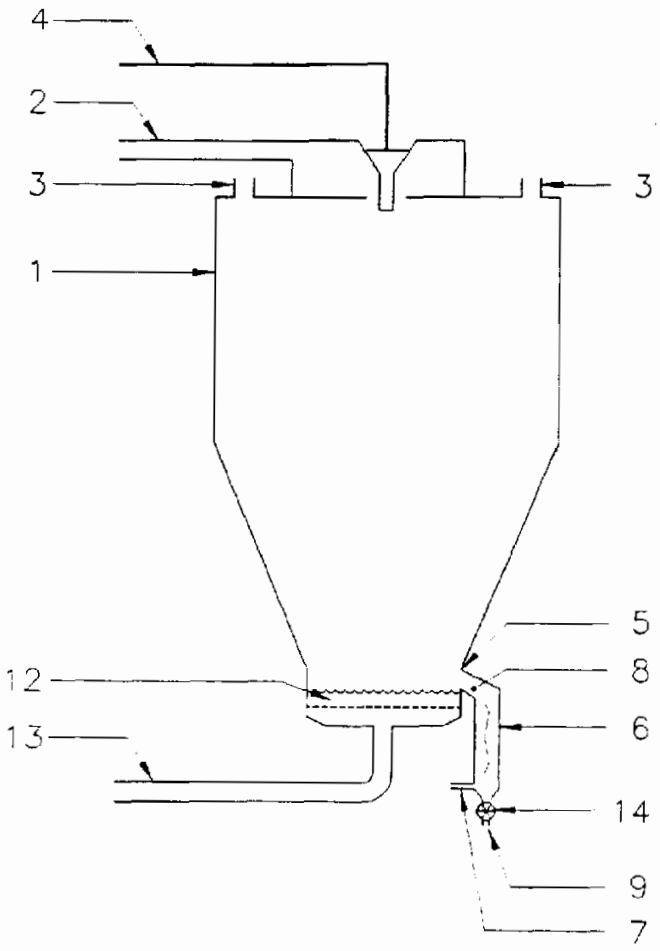
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Fig. 2



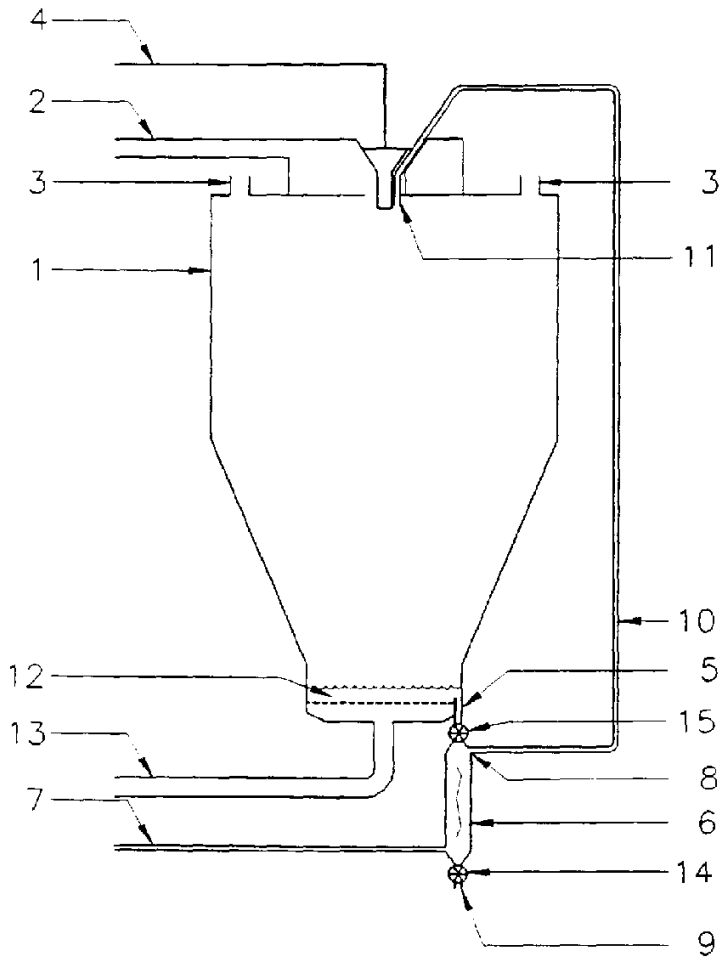
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Fig. 3



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Fig. 4



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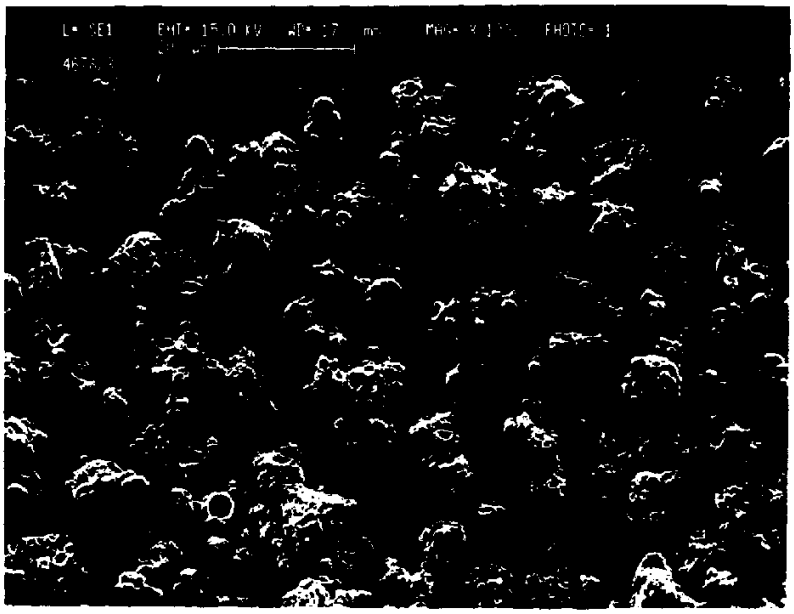


FIG. 5

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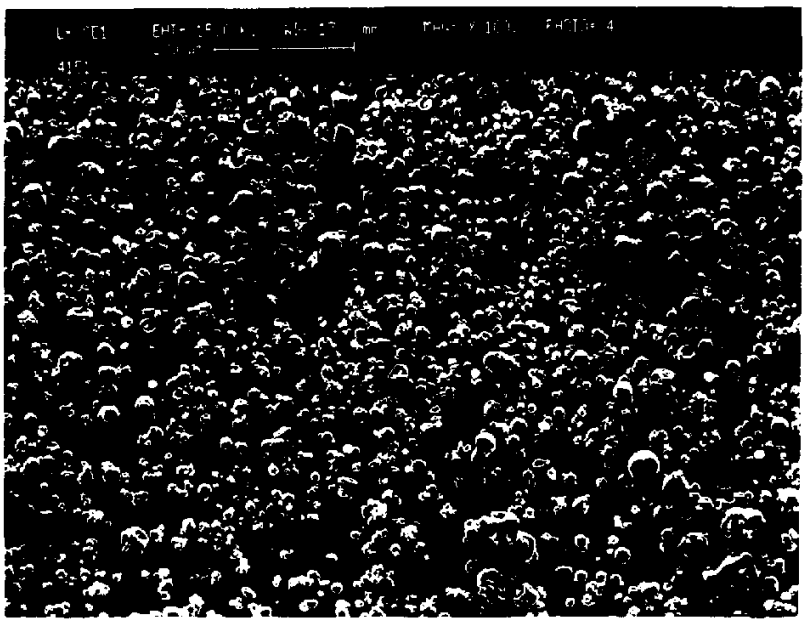
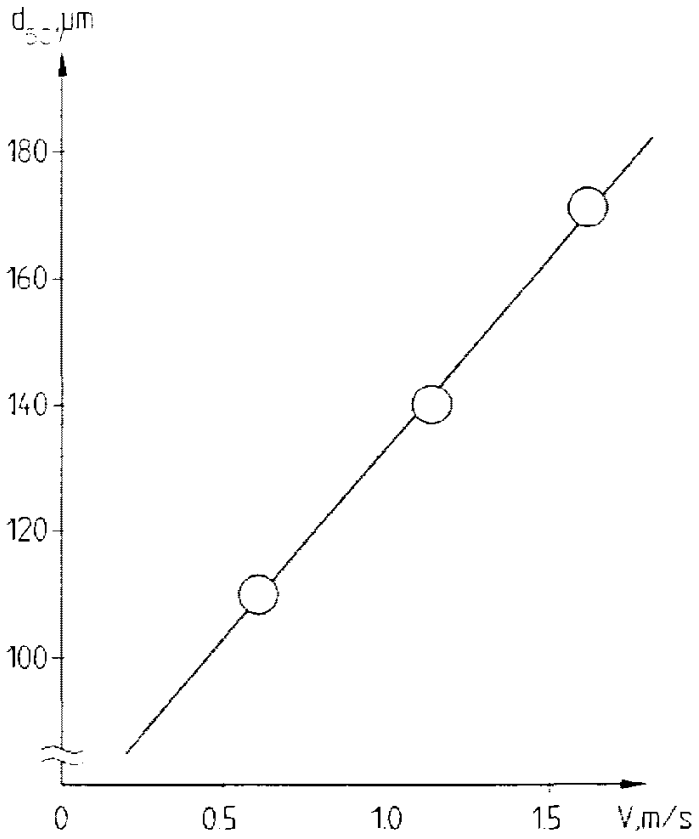


FIG. 6

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Fig. 7



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(54) Readily-dispersible, Hydrocolloid containing agglomerates and process therefor.

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PATENT ABSTRACTS OF JAPAN vol. 9, no. 112 (C-281)(1835) 16 May 1985

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Description

BACKGROUND OF THE INVENTION

The present invention relates to a dry hydrocolloid-containing composition that when hydrated readily disperses in cold aqueous fluids, such as water or milk. This invention is particularly useful in the production of dry dessert mixes, such as instant pudding mixes, and has particular use for the production of dry, sugar-free, instant pudding mixes.

It has long been known that dry, water-gellable/viscosity-building, hydrocolloid food materials, such as pectin, gelatin, pregelatinized starch and vegetable gums, disperse and hydrate in cold water or milk only with difficulty. The use of finely ground particles of these materials has been tried in order to increase surface area, increase the rate of hydration and improve texture (i.e., smoothness) of the prepared food product. Unfortunately, the presence of these fine particles has led to another problem -- namely, clumping of the particles when they are combined with cold water or milk. With these problems in mind the prior art has sought techniques to enable both hydration and dispersion of hydrocolloid materials. These techniques have included use of various dispersants, surfactants, wetting agents, bulking agents as well as various blending and agglomeration techniques. Illustrative of this prior art are U.S. Patents 2,819,970 to Steigmann (fine-grind gelatin coated with a dispersant), 2,819,971 to Gunthardt (fine-grind gelatin coated with lecithin), 3,364,036 to Tesko et al. (fine-grind gelatin coated with triacetin), 3,443,990 to Decnop (heating and drying a mixture of gelatinized starch and a glyceride), 3,582,350 to Werbin et al. (heating and drying an aqueous slurry of pregelatinized starch and a hydrophopic shortening material), 3,987,207 to Spaeti et al. (mixing oil or fat-coated particles of pregelatinized starch material with a dispersion aid and agglomerating with water), 4,016,337 to Hsu (coagglomerating pregelatinized starch and silicon dioxide and coating with a fat-glycerol emulsion), 4,491,483 to Dudacek et al. (a heat and moisture treated starch and fatty acid surfactant product), 4,663,177 to Weaver et al. (sugar-free instant pudding mix containing a non-sugar bulking/dispersing agent), 4,769,081 to Maher (use of a glyceride surfactant to increase starch dispersibility), 4,871,398 to Katcher et al. (a continuous process for producing agglomerated spray-dried starch), and 4,969,955 to Rudin (pregelatinized starch coated with a food grade emulsifier).

The use of fine-grind starch in sugar-containing instant pudding mixes is disclosed in U.S Patents 4,361,592 to Carpenter et al., 4,438,148 to O'Rourke et al. and 4,469,712 to Katcher et al. The presence of the large amount of sugar present in these prior art mixes will prevent clumping of the fine-grind starch upon combining the pudding mix with cold milk. In a sugar-free product, such as disclosed in U.S. Patent 4,695,474 to Cuneo et al., relatively-coarse particle sized starch is employed.

SUMMARY OF THE INVENTION

A readily-dispersible, hydrocolloid-containing food material is produced by spraying fine particles of the hydrocolloid with an aqueous solution of a wetting agent and to agglomerate and spray-coat the particles. The agglomerated material produced in accordance with this invention is surprisingly easy to disperse in cold aqueous fluids, such as cold milk or water. The material can be essentially completely dispersed into a cold aqueous fluid by means of a wire whisk in less than one minute, even in cases where the agglomerate is comprised of only the hydrocolloid material and wetting agent. Where the agglomerate also contains a filler material, such as sugar, maltodextrin, cocoa, etc., the agglomerate can be essentially completely dispersed in the cold fluid by means of only spoon stirring in less than one minute.

This invention is particularly applicable to particles of pregelatinized starch wherein the agglomerates are utilized as an ingredient in instant pudding mixes, instant gravies and sauces, instant cereals and the like. The pregelatinized starch agglomerates are surprisingly functional even in sugar-free instant pudding mixes where the absence of sugar particles has made dispersibility of pregelatinized starch a notorious problem.

Although exemplified primarily in terms of pregelatinized starch, this invention is also useful for producing dispersible particles of other food hydrocolloids such as pectin, gelatin and polysaccharide gums, such as gellan, carrageenan, alginate, guar, etc.

The wetting agent must be a water-soluble, food-acceptable ingredient with little or no emulsifying capability and with no objectionable flavor. Emulsification properties are undesirable in the wetting agent in order to minimize or eliminate interactions with lipid fractions (e.g., milk fat) which may be present in the prepared food product. Typical of such materials are triacetin, glycerol, propylene glycol and tributyrin. The aqueous wetting agent solution will preferably contain from 0.1 to 7% wetting agent by weight of the solution and be sprayed onto the material being agglomerated at a level of 0.1 to 3% wetting agent by

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weight of the hydrocolloid in the material being agglomerated. Desirably, all of the wetting agent will be dissolved in the solution; however, some undissolved wetting agent can be tolerated.

Agglomeration may be effected in either a continuous or batch manner. The type of agglomerator is not critical and equipment such as fluidized bed or tower agglomerators are suitable. The agglomerated material should have a moisture content of less than about 10%, typically 7 to 9%, by weight. Reduction of moisture content can occur entirely within the agglomeration apparatus or, if needed or desired, a separate drying step may be employed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to production of a hydrocolloid-containing, readily-dispersible, food agglomerate which can be characterized as a "friable" agglomerate. In accordance with this invention "friable" is intended to mean that the agglomerate contains internal voids and that the particles which constitute the agglomerate are merely tacked together such that upon mixing with water or milk, or upon compression, such as might be effected by rubbing the agglomerate between the thumb and forefinger, the agglomerate will break apart into essentially the pre-agglomerate sized particles. The agglomerates must of course have sufficient strength to resist attrition during the conveying and blending that is normally experienced by dry food mix ingredients.

The hydrocolloid material (e.g., pregelatinized starch, pectin, etc.) to be agglomerated should preferably have a particle size distribution of 0.5% maximum on a 140 mesh U.S. sieve (106 µm) and 15% minimum on a 400 mesh U.S. sieve (38 µm). More preferred particle size distributions, especially for pregelatinized starch, are as set forth in the aforementioned Katcher et al. patent (4,469,712) wherein between 1 to 10%, preferably 1.5 to 10%, by weight of the particles have a particle size greater than about 63 microns (230 U.S. mesh), less than 1%, preferably less than 0.5%, by weight is greater than about 105 microns (140 mesh), less than 3%, preferably less than 2%, is greater than about 88 microns (170 mesh) and less than 6% is greater than about 74 microns (200 mesh). Most preferably wherein about 6% to about 34% by weight of the particles have a particle size between about 38 microns (400 mesh) and 44 microns (325 mesh) and between about 3% and about 30% of the particles have particle sizes between about 44 microns (325 mesh) and 63 microns (230 mesh). Other hydrocolloid materials can also have these preferred particle size distributions. All particle size analysis used to describe this invention were conducted using an Alpine™ sieve apparatus, a piece of equipment well-known in the food industry.

If the ground hydrocolloid particles are to be co-agglomerated with water-soluble materials which are readily-dispersible, such as sugar, it is not necessary to grind these other materials to the fineness of the hydrocolloid particles. These particles should not be so large, however, that they preclude the formation of stable, properly-sized agglomerates.

The level of wetting agent which is applied to the surface of the materials being agglomerated is about 0.1 to 3%, preferably 0.2 to 1%, of the wetting agent by weight of the hydrocolloid material. Typically the wetting agent solution is sprayed onto the material being agglomerated over an extended period of time, which in the case of batch agglomeration procedures might be for a major part of the agglomeration period.

The agglomeration process is conducted to produce "friable" agglomerates typically having a particle size weight distribution wherein there is a 90% maximum through a 60 U.S. mesh sieve (250 µm), 50% maximum through a 100 U.S. mesh sieve (150 µm) and 10% maximum through a 270 U.S. mesh sieve (53 µm). A preferred agglomerate size distribution is 25 to 55% through a 100 U.S. mesh sieve (150 µm) and 0 to 8% through a 270 U.S. mesh sieve (53 µm). Agglomeration according to this invention should result in a bulk density reduction of at least 50%. In the case of agglomerates which consist essentially of ground hydrocolloid particles the density of the agglomerate should be from 0.1 to 0.3g/cc, and for pregelatinized starch preferably from 0.14 to 0.20g/cc. A suitable material for use in this invention is pregelatinized, spray-dried dent, cornstarch, such as fully-described in U.S. Patent No. 4,847,371 to Schara and Katcher. Spray-dried or solvent processed starches that are essentially in whole granule form when hydrated, such as those described in U.S. Patent Nos. 4,280,851 to Pitchon et al, 3,563,798 to Germino et al, 3,617,383 to Thurstan et al, and 3,705,891 to Tuschoff et al, may also be readily utilized in the process of this invention. Any pregelatinized starch that hydrates in a cold liquid to essentially 100% swollen whole granules will be useful for this invention.

As shown in the examples below, a readily-dispersible starch agglomerate is produced which can be used in making a creamy, smooth instant dessert having a shiny surface and a greatly reduced incidence of visual lumps. Attempts to prepare a comparable starch agglomerate using water alone, without the presence of the wetting agent, resulted in a starch material that had somewhat increased dispersibility, as compared to unagglomerated, unground starch, but which when used in an instant pudding mix produced a grainier

textured pudding. Spraying a wetting agent, such as triacetin, onto the surface of a water-agglomerated fine grind starch did not improve performance of the starch in instant pudding mixes. Merely spraying a wetting agent, such as triacetin, onto the surface of fine-grind starch does not result in a readily-dispersible starch material. Although the starch material is described primarily in terms of spray-dried starch, other types of pregelatinized starch (e.g. drum dried) may also be employed.

This invention is further described but not limited by the following examples:

EXAMPLE 1

300g of ground spray-dried cornstarch, as disclosed in the Schara and Katcher patent, was added to a benchtop-scale, fluid-bed agglomerator (Aeromatic Strea 1, mfg. by Aeromatic, Inc. Columbia, Maryland). The particle size distribution of the starch was less than 0.5% on a 140 U.S. mesh screen (106 µm) and at least 15% on a 400 U.S. mesh screen (38 µm). The starch was preheated to an air inlet temperature of 80°C after which agglomeration of the starch was effected via application of a 1% solution of triacetin applied at a constant rate of 180g over 20 minutes. After 20 minutes, the spray was stopped but fluidization of the bed with the 80°C air flow was continued for another 2 minutes to reduce the moisture of the agglomerate to about 8%.

The resulting starch agglomerate had a bulk density of about .16g/cc, was friable and had a particle size distribution of 75-85 through a 60 U.S. mesh screen (250 µm), 25-55% through a 100 U.S. mesh screen (150 µm) and 0.8% through a 270 U.S. mesh (53 µm).

EXAMPLE 2

An instant, chocolate-flavored dessert mix was formulated as follows:

Agglomerated Starch (Example 1)	21g
Maltodextrin (10 D.E.)	10g
Disodium phosphate	1.5g
Tetrasodium Pyrophosphate	1.5g
Cocoa	12g
Aspartame	as desired
Flavor/Color	as desired

This mix was added to two cups of cold milk and mixed with a wire whisk for one minute at which time the mix had essentially completely dispersed. Upon setting, a smooth, creamy pudding was obtained which was completely lump-free.

EXAMPLE 3

The procedure of Examples 1 and 2 were repeated utilizing a drum-dried, pregelatinized tapioca starch having a somewhat coarser particle size distribution. The agglomerate produced was equivalent in size to that of Example 1 and the instant pudding produced was acceptable and lump-free.

EXAMPLE 4

9 pounds of ground, pregelatinized cornstarch, as in Example 1, was placed in a Glatt™ 5/9 Agglomerator (mfg. by Air Techniques, Inc. Ramsey, New Jersey) and preheated to 40°C (with air having an inlet air temperature of 70°C). 2800g of a 1.5% triacetin solution was applied at a constant rate over a 33 minute period to effect agglomeration. The agglomerated starch was passed through a 30 U.S. mesh screen (600 µm) to remove undesirable coarse particles prior to being added to an instant pudding mix.

EXAMPLE 5

200g of finely-ground pectin (100% through a 200 U.S. mesh [75 µm], less than 65% on 400 U.S. mesh [38 µm]) was added to the benchtop-scale, fluid-bed agglomerator of Example 1. The pectin was preheated with heated air having an inlet temperature of 80°C. Agglomeration was accomplished via spray application of a 2% solution of triacetin in water applied at a constant rate of 150g over 18 minutes. The resulting

agglomerated pectin had a particle size distribution of 100% through U.S. 40 mesh (425 µm), less than 45% through 140 U.S. mesh (106 µm), and less than 10% through 270 U.S. mesh (53 µm). The bulk density of the agglomerated pectin after sieving through a 40 U.S. mesh screen (425 µm) was 0.28 g/cc and the pectin was readily dispersible in cold tap water using a fork within 45 seconds.

EXAMPLE 6

500g of a vanilla instant pudding mix as set forth below was agglomerated as in Example 5 using a 1% triacetin solution applied at a rate to result in 101 to 135 of solution applied over 11 to 11.5 minutes.

Sugar	76.2g
Pre-Gelatinized Starch (as in Example 1)	19.5g
Tetrasodium Pyrophosate	1.75g
Disodium Phosphate	1.75g
Mono and Diglycerides	0.5g
Vanilla Flavor/Color	as desired

The agglomerated pudding mix when added to 2 cups of cold milk dispersed by stirring with a spoon within 30 seconds.

Claims

1. A method for producing a friable agglomerate consisting essentially of fine particles of a hydrocolloid and a wetting agent wherein said hydrocolloid is selected from the group consisting of pregelatinized starch, pectin, gelatin, polysaccharide gums and combinations thereof and wherein said wetting agent has little or no emulsifying capabilities comprising the steps of:
   (a) obtaining fine particles of said hydrocolloid, said particles having a size distribution of 0.5% by weight maximum on a 140 U.S. mesh sieve (106 µm) and 15% by weight minimum on a 400 U.S. mesh sieve (38 µm);
   (b) spraying the particles with a wetting agent to a level of 0.1 to 3% wetting agent by weight of the hydrocolloid and agglomerating the sprayed particles; and
   (c) drying the agglomerates to a moisture content of less than about 10% by weight.

2. A method according to claim 1, wherein the wetting agent is selected from the group consisting of triacetin, glycerol, propylene glycol, tributyrin, and mixtures thereof.

3. A method according to claim 2, wherein the particles are sprayed with an aqueous triacetin solution containing from 0.1 to 7% wetting agent by weight of solution.

4. A method according to any one of claims 1 to 3, wherein the hydrocolloid is a pregelatinized starch which hydrates in a cold liquid to essentially 100% swollen whole starch granules.

5. A method according to claim 4, wherein the pregelatinized starch is a spray-dried pregelatinized starch.

6. A method according to claim 5, wherein the fine starch particles are particles of ground, spray-dried pregelatinized starch having a particle size distribution of less than 3% greater than 170 U.S. mesh sieve (90 µm) and less than 6% greater than 200 U.S. mesh sieve (75 µm).

7. A method according to any one of claims 1 to 6, wherein the level of wetting agent is from 0.5 to 2% by weight of the hydrocolloid material.

8. A method according to any one of claims 1 to 7, wherein the sprayed particles are agglomerated in a fluidized bed or tower agglomerator.

9. Readily-dispersible, friable agglomerates consisting essentially of finely-ground pregelatinized starch particles and a wetting agent which has little or no emulsifying capabilities wherein the agglomerates have a bulk density of from 0.1 to 0.3g/cc and a particle size distribution of maximum 90% by weight

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through a 60 U.S. mesh sieve (250 µm) and a maximum of 10% by weight through a 270 U.S. mesh sieve (53 µm), wherein the starch particles formed into the agglomerate have a particle size distribution of 0.5% by weight maximum on a 140 U.S. mesh sieve (106 µm) and 15% by weight minimum on a 400 U.S. mesh sieve (38 µm) and the bulk density of the starch is reduced by at least 50% as a result of agglomeration, and wherein the wetting agent is spray-coated onto the surface of the starch particles being agglomerated at a level of from 0.1 to 3% by weight of the starch.

10. A sugar-free, instant powdered food mix comprised of from 40 to 60% of the agglomerates of claim 9, a carbohydrate bulking agent, an intensive sweetener, flavor and color.

11. A sugar-free food mix according to claim 10, wherein the food mix is an instant dessert mix and additionally contains phosphate setting salts.

Patentansprüche

1. Verfahren zur Herstellung eines bröckeligen Agglomerats, das im wesentlichen aus feinen Partikeln eines Hydrokolloids und einem Benetzungsmittel besteht, worin genanntes Hydrokolloid aus der Gruppe ausgewählt wird, die aus vorverkleisterter Stärke, Pektin, Gelatine, Polysaccharidgummen und Kombinationen davon besteht und worin genanntes Benetzungsmittel wenig oder keine Emulgierfähigkeiten besitzt, das die folgenden Schritte umfaßt:

(a) Gewinnung feiner Partikel von genanntem Hydrokolloid, worin genannte Partikel eine Größenverteilung von maximal 0,5 Gew.-% auf einem 140-Mesh-Sieb nach U.S.-Standard (106 µm) und minimal 15 Gew.-% auf einem 400-Mesh-Sieb nach U.S.-Standard (38 µm) aufweisen;

(b) Besprühen der Partikel mit einem Benetzungsmittel bis zu einem Anteil von 0,1 bis 3 Gew.-% Benetzungsmittel bezogen auf das Hydrokolloid und Agglomerieren der besprühten Partikel; und

(c) Trocknen der Agglomerate auf einen Feuchtigkeitsgehalt von weniger als circa 10 Gew.-%.

2. Verfahren nach Anspruch 1, worin das Benetzungsmittel aus der Gruppe ausgewählt wird, die aus Triacetin, Glycerol, Propylenglycol, Tributyrin und Gemischen davon besteht.

3. Verfahren nach Anspruch 2, worin die Partikel mit einer wäßrigen Triacetinlösung besprüht werden, die von 0,1 bis 7 Gew.-% Benetzungsmittel bezogen auf die Lösung enthält.

4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Hydrokolloid eine vorverkleisterte Stärke ist, die in einer kalten Flüssigkeit zu im wesentlichen 100% gequollenen ganzen Stärkekörnchen hydratisiert.

5. Verfahren nach Anspruch 4, worin die vorverkleisterte Stärke eine sprühgetrocknete vorverkleisterte Stärke ist.

6. Verfahren nach Anspruch 5, worin die feinen Stärkepartikel Teilchen aus gemahlener sprühgetrockneter vorverkleisterter Stärke mit einer Partikelgrößenverteilung von weniger als 3% größer als 170-Mesh-Sieb nach U.S.-Standard (90 µm) und weniger als 6% größer als 200-Mesh-Sieb nach U.S.-Standard (75 µm) sind.

7. Verfahren nach einem der Ansprüche 1 bis 6, worin der Anteil des Benetzungsmittels von 0,5 bis 2 Gew.-% des Hydrokolloidmaterials beträgt.

8. Verfahren nach einem der Ansprüche 1 bis 7, worin die besprühten Partikel in einem Wirbelbett oder Agglomerationsturm agglomerisiert werden.

9. Leicht dispergierbare, bröckelige Agglomerate, die im wesentlichen aus feingemahlenen vorverkleisterten Stärkepartikeln und einem Benetzungsmittel bestehen, das wenig oder keine Emulgierfähigkeiten besitzt, worin die Agglomerate eine Fülldichte von 0,1 bis 0,3 g/cc und eine Partikelgrößenverteilung von maximal 90 Gew.-% durch ein 60-Mesh-Sieb nach U.S.-Standard (250 µm) und maximal 10 Gew.-% durch ein 270-Mesh-Sieb nach U.S.-Standard (53 µm) aufweisen, worin die zum Agglomerat geformten Stärkepartikel eine Partikelgrößenverteilung von maximal 0,5 Gew.-% auf einem 140-Mesh-Sieb nach U.S.-Standard (106 µm) und minimal 15 Gew.-% auf einem 400-Mesh-Sieb nach U.S.-

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Standard (38 µm) aufweisen und die Fülldichte der Stärke aufgrund von Agglomeration um mindestens 50% vermindert ist und worin das Benetzungsmittel auf die Oberfläche der Stärkepartikel, die bei einem Anteil von 0,1 bis 3 Gew.-% der Stärke agglomeriert sind, sprühaufgetragen wird.

10. Zuckerfreies Instantpulver-Nährmittelgemisch, das aus 40 bis 60% der Agglomerate nach Anspruch 9, einem Kohlenhydratfüllmittel, einem Intensivsüßstoff, Geschmacks- und Farbstoff besteht.

11. Zuckerfreies Nährmittelgemisch nach Anspruch 10, worin das Nährmittelgemisch ein Instantdessert-Mix ist und außerdem Phosphaterstarrungssalze enthält.

Revendications

1. Méthode pour produire un agglomérat friable composé essentiellement de particules fines d'un hydrocolloïde et d'un agent mouillant dans laquelle ledit hydrocolloïde est sélectionné dans le groupe composé d'amidon prégélatinisé, pectine, gélatine, gommes de polysaccharides et combinaisons de ceux-ci et dans laquelle ledit agent mouillant a peu ou pas de capacités émulsionnantes comprenant les étapes de:

(a) obtention de particules fines dudit hydrocolloïde, lesdites particules ayant une distribution granulométrique de 0,5% en poids maximum sur un écran américain de 140 meshs (106 µm) et 15% en poids minimum sur un écran américain de 400 meshs (38 µm);

(b) vaporisation des particules avec un agent mouillant jusqu'à un niveau de 0,1 à 3% d'agent mouillant en poids de l'hydrocolloïde et agglomération des particules vaporisées; et

(c) séchage des agglomérats jusqu'à un contenu d'humidité inférieur à environ 10% en poids.

2. Méthode selon la revendication 1, dans laquelle l'agent mouillant est sélectionné dans un groupe constitué de triacétine, glycérol, propylèneglycol, tributyrine, et des mélanges de ceux-ci.

3. Méthode selon la revendication 2, dans laquelle les particules sont vaporisées avec une solution de triacétine acqueuse contenant de 0,1 à 7% d'agent mouillant en poids de solution.

4. Méthode selon l'une quelconque des revendications 1 à 3, dans laquelle l'hydrocolloïde est un amidon prégélatinisé qui s'hydrate dans un liquide froid en essentiellement des grains d'amidon entiers gonflés à 100%.

5. Méthode selon la revendication 4, dans laquelle l'amidon prégélatinisé est un amidon prégélatinisé séché par pulvérisation.

6. Méthode selon la revendication 5, dans laquelle les particules fines d'amidon sont des particules d'amidon prégélatinisé séché par pulvérisation, broyé, ayant une distribution granulométrique de particules de moins de 3% supérieure à l'écran américain de 170 meshs (90 µm) et de moins de 6% supérieure à l'écran américain de 200 meshs (75 µm).

7. Méthode selon l'une quelconque des revendications 1 à 6, dans laquelle le niveau d'agent mouillant est de 0,5 à 2% en poids de la matière hydrocolloïde.

8. Méthode selon l'une quelconque des revendications 1 à 7, dans laquelle les particules vaporisées sont agglomérées dans un lit fluidisé ou une tour d'agglomération.

9. Agglomérats friables, aisément dispersables, composés essentiellement de particules d'amidon prégélatinisé finement broyé et d'un agent mouillant qui a peu ou pas de capacités émulsionnantes dans lesquels les agglomérats ont une densité volumique en vrac allant de 0,1 à 0,3g/cc et une distribution granulométrique de particules de 90% maximum en poids à travers un écran américain de 60 meshs (250 µm) et de 10% maximum en poids à travers un écran américain de 270 meshs (53 µm), dans lesquels les particules d'amidon formées dans l'agglomérat ont une distribution granulométrique de particules de 0,5% en poids maximum sur un écran américain de 140 meshs (106 µm) et de 15% en poids minimum sur un écran américain de 400 meshs (38 µm) et la masse volumique en vrac de l'amidon est réduite d'au moins 50% à la suite de l'agglomération, et dans lesquels l'agent mouillant est appliqué au pistolet sur la surface des particules d'amidon étant agglomérées à un niveau de 0,1 à

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3% en poids de l'amidon.

10. Préparation alimentaire instantanée en poudre, sans sucre, composée à raison de 40 à 60% des agglomérats de la revendication 9, d'un agent de charge de glucides, d'un édulcorant intensif, d'un arôme et d'un colorant.

11. Une préparation alimentaire sans sucre selon la revendication 10, dans laquelle la préparation alimentaire est une préparation pour dessert instantanée et contient en outre des sels de prise de phosphate.

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(54) Improved drying of acid whey and/or acid permeate

Verbesserte Trocknung von saurer Molke und/oder saurem Permeat

Séchage amélioré de lactosérum acide et/ou de perméat acide

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- **JOURNAL OF DAIRY SCIENCE. vol. 61, no. 3 , 1978 , CHAPAIGN, ILLINOIS US pages 294 - 299 H. MODLER ET AL. 'Calcium as an adjuvant for spray-drying acid whey'**
- **DATABASE WPI Week 7708, 1976 Derwent Publications Ltd., London, GB; AN 77-14246Y & SU-A-488 578 (BUTTER CHEESE IND)**

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to an improved process for drying of acid whey and/or acid whey permeate. More particularly, the present invention relates to a process for spray drying the acid type of cheese whey or casein, partially delactosed acid whey or an acid permeate obtained by ultrafiltration of acid whey and/or acid cheese milk. This is accomplished by injecting a dry neutralizing edible calcium or magnesium salt during the spray drying of the acid whey and/or permeate products and drying the resulting product.

DESCRIPTION OF THE PRIOR ART

It is well known that the spray drying technology leads to severe clogging of the spray tower and the associated cyclone if acid whey and/or acid permeate are spray dried. This situation results in very short running times and therefore, makes it impossible to handle the increasing amount of acid whey and/or acid permeate resulting from fresh cheese production. The fouling and clogging within the spray tower can be partly reduced by adding approximately 30 to 40% by weight of sweet whey to the acid mix or adding a lesser amount of sweet whey with an inert anti-caking agent.

US-A-3840996 suggests adding a drying agent, such as tricalcium phosphate or dicalcium phosphate, to the main drying chamber, such as a spray dryer, during drying of a mineral containing aqueous protein solution, such as acid or sweet cheese whey or a modified cheese whey. When using a low molecular weight fraction obtained from the molecular sieve resin separation of cheese whey, it is taught to use a solids content between about 25 percent to about 35 percent weight basis. It is further described how the drying agent is added at a solids feed rate equivalent to between about 1 percent to about 10 percent by weight of modified cheese whey solids as feed into the dryer.

FR-A-2212101 describes a treatment agent which can be added as a powder in the atomization tower during spray-drying of whey. This treatment agent contains 1 to 25% finely divided silica, 5 to 60% of at least one alkaline earth metal salt of a natural fatty acid, and 30 to 80% of magnesium oxide or magnesium hydroxide.

In an article entitled "Calcium as an Adjuvant for Spray-Drying Acid Whey" by H.W. Modler and D.B. Emmons, J. Dairy Sci 61:294-299, there is described a series of experiments in which acid whey with a solids content maintained at approximately 22 to 24% was subjected to spray-drying in a pilot plant dryer. In these experiments CaO and/or $CaCl_2$ were added to the whey before spray-drying. Although the treated whey dries easily, the product was described as chalky, bitter, and stringent with a high solubility index. Clarification using a desludging centrifuge greatly improved flavor, decreased solubility index, increased product clarity upon reconstitution, decreased ash content, and reduced wear on drying equipment.

Other methods used include that described in US-A-3615644 which utilizes a process for demineralization of a high heat treated delactosed whey and also provides whey processing steps to improve drying characteristics of the material. This is accomplished by crystallizing the liquid whey product and removing the lactose crystals. The resulting whey is clarified and adjusted to a pH of 3.9 to 4.2 for cheddar cheese whey and 4.65 to 6.5 for sweet whey, subjecting the clarified whey to electrodialysis, concentrating the electrodialyzed material and spray drying the resulting product. US-A-4057655 describes a process for preparing a free flowing lactulose-containing powder from whey solutions or permeates by adding calcium hydroxide to adjust the pH to 9.4 to 11.2, heating the solution to reduce the pH to 7.5 to 9, then homogenizing, concentrating and drying the resultant product. This patent refers to the use of calcium hydroxide for conversion of lactose into lactulose. US-A-4088791 describes a process for making a free flowing modified whey powder by forming an emulsion of titanium dioxide, fat and water, neutralizing (pH 6.7 to 7.4) the emulsion and adding the emulsion to a concentrated whey and spray drying the product. The neutralization step is accomplished by the addition of calcium lactate or a combination of calcium carbonate or calcium hydroxide, aluminium hydroxide and magnesium carbonate.

SUMMARY OF THE INVENTION

The process of the present invention is a process for spray drying a dairy product selected from acid whey and products derived from acid whey comprising concentrating said product by evaporation, feeding said dairy product into a spray dryer and injecting into said spray dryer up to 10% by weight of the finished product of a dry edible salt and drying the resulting product, characterized in that the dairy product contains crystallized lactose, is selected from acid whey, acid whey permeate and acid cheese milk permeate, and has been concentrated to a concentration in the range of 45% to 60% by weight solids without prior neutralization, and that the dry edible salt is a dry neutralizing edible salt selected from calcium hydroxide, calcium carbonate, calcium oxide, magnesium hydroxide, magnesium carbonate, magnesium oxide and mixtures thereof and is injected in an amount of from 0.5% to 10% by weight of the finished product. This process is a simple process without the need of using multiple steps, does not require the addition of a sweet whey or sweet permeate (although small amounts of sweet whey or sweet permeate can be present) and the spray drying process can be conducted for extended periods of time without clogging and fouling of the tower.

DETAILED DESCRIPTION OF INVENTION

The raw material used in the present invention is a by-product solution from dairy plants predominantly containing lactose. The by-product solution includes whey from the manufacture of cheese such as cottage cheese, cream cheese and the like, known in the industry as acid whey, which is difficult to crystallize and even when crystallized, is difficult to dry into a non-sticky, free flowing powder. It also includes the ultrafiltration permeates from acid cheese milks and/or whey.

So troublesome is the drying of acid whey and/or dairy permeates that most producers of cottage cheese and cream cheese do not even attempt to dry their whey. It is simply disposed of in a waste water treatment system or hauled away, sometimes concentrating it to reduce its volume before hauling.

Ordinary whey is classified according to its lactic acid content into the categories of acid whey having a titratable acidity not less than 0.40% and sweet whey having a titratable acidity of not greater than 0.16%. In this invention the acid whey can be of the type obtained from cheese or casein, partially delactosed acid whey or permeate obtained by ultrafiltration of acid whey and/or acid (synthetic cultures sour) cheese milk.

Prior to feeding the acid whey and/or acid permeate into the spray dryer, these materials are concentrated by evaporation to 45 to 60% by weight solids forming a paste-like material. This paste-like material is stored for a period of time to allow the crystallization of most of the lactose. The resulting paste is fed into the spray dryer maintained at temperatures in the range from 110°C to 200°C to produce a dry powder leaving the spray tower having a moisture content of 10 to 30% by weight. A subsequent heating step is provided to dry the powder to levels from 2 to 5 weight % moisture. The essential element to this invention is during the drying procedure, a dry neutralizing edible calcium or magnesium salt is injected into the spray dryer blending with the acid whey and/or acid permeate in amounts from 0.5 to 10% by weight, preferably 0.5% to 5% by weight of the total contents of the finished product. The amount of the dry neutralizing edible calcium or magnesium salt results in a pH of the final water dissolved whey or permeate powder in the range from 5.8 to 7.0.

The dry neutralizing edible calcium and/or magnesium salts which can be used in this invention are calcium hydroxide, calcium carbonate, calcium oxide, magnesium hydroxide, magnesium carbonate, magnesium oxide, and mixtures thereof.

The significant advantage of this invention is that the injection of the dry neutralizing edible salt into the spray dryer with the acid whey and/or acid permeate containing crystallized lactose, provides a process which is substantially free of clogging and fouling of spray tower and the associated cyclone over extended periods of time for as long as 4 to 5 days or longer.

Utilizing the claimed invention provides a highly desirable spray drying technique for acid permeate from ultrafiltered acid cheese milks or ultrafiltered acid whey which heretofore spray drying of these products was extremely difficult and, in some instances, not possible at all.

The following examples are provided to further illustrate the invention.

EXAMPLE 1

A mixture of 50% weight percent of acid whey and 50 weight percent acid permeate was concentrated to a dry matter of 52.3% (the pH was 4.37) and stored for one day at a temperature of 24°C. The resulting concentrate with partially crystallized lactose was fed into a spray dryer at a flow rate of 1500 liters per hour. The air inlet temperature of the spray dryer was 130°C and the outlet temperature was 53°C. Dry calcium hydroxide, transported by air into the tower, was fed in at a concentration of about 1.3 weight percent of the finished spray dried product. The spray nozzle for the calcium hydroxide was mounted about 1.5 meters under the spraying disc to allow a homogeneous coating of the droplets of the material to be dried. The product then falls into a drum dryer having an inlet temperature of the air of 178°C and an outlet temperature of 101°C. The compositional analysis of the finished product showed the following data:

Total Solids	97.8%
pH Value (7g in 100 ml)	6.15
Fat	1.9%
Protein	5.16%
NaCl	2.69%
Lactose	64.8%
Calcium	2.6%
Lactic Acid	9.73%
Ash	13.0%

Additional trials were conducted neutralizing the acid whey or the acid concentrate prior to spray drying by adding sodium hydroxide and separately calcium hydroxide to the liquid phase to increase the pH from 4.2 to 5.8. During the spray drying, severe clogging within an hour of the tower was observed with both the calcium hydroxide and sodium hydroxide addition to the whey.

In a similar manner, the injection of dry sodium hydroxide into the spray tower did not provide any significant improvement. Also the injection of an aqueous solution of calcium hydroxide to the liquid whey or permeate or its concentrate during spray drying did not provide any improvements compared to the present invention.

Consequently the direct injection of dry, powdered neutralizing edible calcium or magnesium salts into the spray dryer is a key element of the present invention. It provides the optimal reaction conditions to obtain a free-flowing powder. The injection of dry powdered neutralizing calcium salts is believed to instantaneously generate a large internal surface by coating the spray dry ingredients and leads to a general reduction of the water concentration at the surface. This allows optimal and effective crystallization of the lactose into agglomerated particles without clogging. It is further believed that the addition of the dry powdered neutralizing calcium or magnesium salts into the acid whey and/or acid permeate improves the kinetic conditions to achieve an almost complete precipitation of the organic acids such as the insoluble calcium salts of lactic acid, phosphoric acid, and citric acid.

Another effect of the direct powder injection is to keep the heat- and alkali-induced deterioration reactions to a minimum, e.g., formation of lactulose, because of minimum exposure to heat and alkali.

The advantages of this spray drying technology of this invention are as follows:

- spray drying of pure acid whey and/or pure acid permeate without the need for availability of sweet whey
- excellent solubility of the finished whey or permeate powder
- safe handling of the dry calcium salts (compared to aqueous calcium salt solutions).

Claims

1. A process for spray drying a dairy product selected from acid whey and products derived from acid whey comprising concentrating said product by evaporation, feeding said dairy product into a spray dryer and injecting into said spray dryer up to 10% by weight of the finished product of a dry edible salt and drying the resulting product, characterized in that the dairy product contains crystallized lactose, is selected from acid whey, acid whey permeate and acid cheese milk permeate, and has been concentrated to a concentration in the range of 45% to 60% by weight solids without prior neutralization, and that the dry edible salt is a dry neutralizing edible salt selected from calcium hydroxide, calcium carbonate, calcium oxide, magnesium hydroxide, magnesium carbonate, magnesium oxide and mixtures thereof and is injected in an amount of from 0.5% to 10% by weight of the finished product.

2. A process according to claim 1, characterized in that 0.5% to 5% by weight of said dry neutralizing edible salt is injected into said spray dryer.

3. A process according to claim 1 or claim 2, characterized in that said dry edible neutralizing calcium salt is calcium hydroxide.

Patentansprüche

1. Verfahren zum Sprühtrocknen eines Molkereiproduktes, das aus Sauermolke und sich von Sauermolke herleitenden Produkten ausgewählt wird, das folgendes umfaßt: Eindicken von genanntem Produkt durch Verdampfen, Einspeisen von genanntem Molkereiprodukt in einen Sprühtrockner und Einspritzen von bis zu 10 Gew.-% des Fertigproduktes aus einem trockenen, genießbaren Salz in genannten Sprühtrockner und Trocknen des sich ergebenden Produktes, dadurch gekennzeichnet, daß das Molkereiprodukt kristallisierte Lactose enthält, aus Sauermolke, Sauermolkenpermeat und saurem Käsemilchpermeat ausgewählt wird und ohne vorherige Neutralisation auf eine Konzentration im Bereich von 45 Gew.-% bis 60 Gew.-% Feststoffe eingedickt wurde und daß das trockene, genießbare Salz ein trockenes, neutralisierendes, genießbares Salz ist, das aus Calciumhydroxid, Calciumcarbonat, Calciumoxid, Magnesiumhydroxid, Magnesiumcarbonat, Magnesiumoxid und Gemischen davon ausgewählt und in einer Menge von 0,5 Gew.-% bis 10 Gew.-% des Fertigproduktes eingespritzt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß 0,5 Gew.-% bis 5 Gew.-% des genannten trockenen, neutralisierenden, genießbaren Salzes in genannten Sprühtrockner eingespritzt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß genanntes, trockenes, genießbares, neutralisierendes Calciumsalz Calciumhydroxid ist.

Revendications

1. Un procédé pour sécher par pulvérisation un produit laitier sélectionné à partir de lactosérum acide et de produits dérivés de lactosérum acide, comprenant: concentrer ledit produit par évaporation, introduire ledit produit laitier dans un séchoir à pulvérisation et injecter dans ledit séchoir à pulvérisation jusqu'à 10% par poids du produit fini d'un sel comestible sec et sécher le produit qui en résulte, caractérisé en ce que le produit laitier contient du lactose cristallisé, qu'il est sélectionné à partir de lactosérum acide, d'un perméat de lactosérum acide et d'un perméat de lait de fromage acide, et qu'il a été concentré à une concentration dans la gamme de 45% à 60% par poids de solides sans neutralisation préalable et que ledit sel comestible sec est un sel comestible sec neutralisant sélectionné à partir d'hydroxyde de calcium, de carbonate de calcium, d'oxyde de calcium, d'hydroxyde de magnésium, de carbonate de magnésium,

d'oxyde de magnésium et de mélanges des mêmes et est injecté selon une quantité de 0,5% à 10% par poids du produit fini.

2. *Un procédé selon la revendication 1, caractérisé en* ce que de 0,5% à 5% par poids dudit sel comestible sec neutralisant est injecté dans ledit séchoir à pulvérisation.

3. Un procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit sel de calcium comestible sec neutralisant est de l'hydroxyde de calcium.

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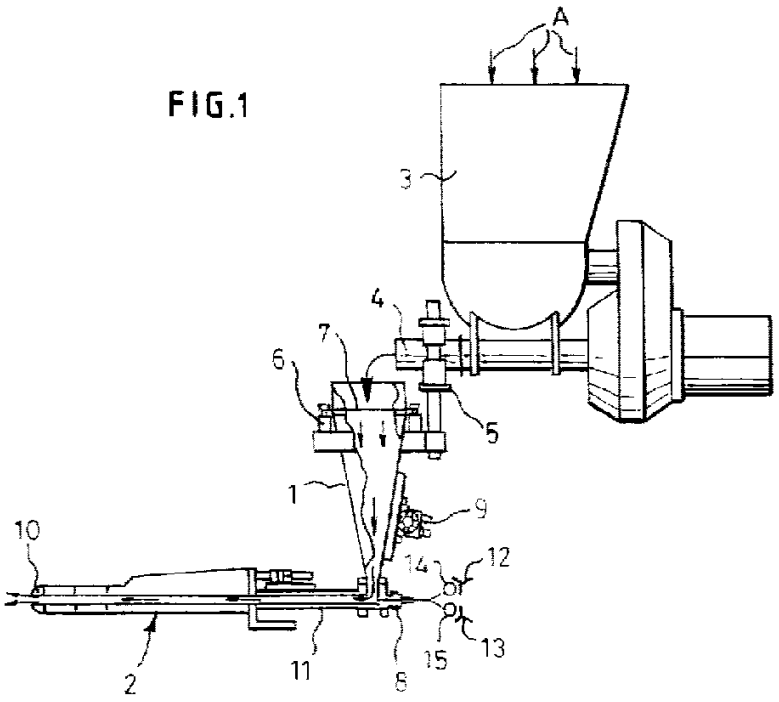
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(54) An electrostratic flavouring system

(57) An electrostatic flavouring system comprises a hopper (1) for receiving a flavouring material from a supply (3, 4). An injector (8) is connected to the outlet of the hopper (1) and an electrostatic spray gun (2) is connected via a hose (11) to the injector (8). Two air feed means (12, 13) are provided for feeding air to the injector (8), the first air means (12) providing air at conveying pressure and the second air means (13) providing air at a higher pressure for the purpose of purging the injector (8) and/or the hose (11) and/or the electrostatic gun (2).

FIG.1



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Description

This invention relates to an electrostatic flavouring system and is an improvement in our co-pending application no GB 2277469A.

In that application, there is described an electrostatic system for power coating products comprising a container for the powder, a pump unit for pumping powder from the container to an electrostatic powder gun under the control of a powder gun control unit in which a venturi and hose rinsing pulsation control is connected through a venturi to a hose leading to the powder gun to purge any build up of powder in the venturi, hose or powder gun.

A number of electrostatic apparatuses are known for coating food products, such as snacks, with powdered flavouring. The powdered flavouring may contain dispersed oil or it may be formed with animal fats such as cheese. This has the disadvantage that the oil or fat may build up in the system tubes and the electrostatic gun with the result that agglomerations of powder may become dislodged and caused to adhere to the food snacks in lumps resulting in unpleasant concentrations of the flavouring powder on the food snacks and consequent adverse customer reaction. To prevent this, the system requires regular cleaning and maintenance, particularly when changing the powdered flavouring to provide a different flavoured coating.

The present invention seeks to provide an improved electrostatic system which assists in the free flow of powder through the system.

According to the invention, there is provided an electrostatic flavouring system comprising a hopper for receiving a flavouring material from a supply, an injector connected to the outlet of the hopper, an electrostatic spray gun connected via a hose to the injector and two air feed means for feeding air to the injector, the first air means providing air at conveying pressure and the second air means providing air at a higher pressure for the purpose of purging the injector and/or the hose and/or the electrostatic gun.

Preferably, both air feed means feed into a single inlet in the injector. One or both of the air feeds means may have a non return valve.

A vibrator may be clamped to the hopper or the hopper may be connected to a support arm through a vibrator.

A screw feeder may be arranged to feed the flavouring material into the upper part of the hopper.

The invention will now be described in greater detail, by way of example, with reference to the drawings, in which:-

Figure 1 is a diagrammatic cross-sectional view of one form of the electrostatic flavouring system according to the invention, and

Figure 2 is a fragmentary cross-sectional view of a modified feed system.

Referring firstly to figure 1, a feed hopper 3 is provided for receiving flavouring powder in the direction A. Powder from this feed hopper 3 is fed at a metered rate by means of a screw feeder 4 into which the outlet from the feed hopper 3 feeds.

The outlet of the screw feeder 4 feeds into a dispersion hopper 1, suitably mounted directly on to the screw feeder 4 by suitable clamping means indicated at 5, the clamping means preferably being of a vibration insulating type to minimize the transmission of vibrations from the dispersion hopper 1.

The flavouring powder from the screw feeder 4 passes into the dispersion hopper 1 by way of a sieving grid 7 which breaks up any conglomerations of the flavouring powder which might otherwise enter the dispersion hopper 1. An injector 6 is located at the outlet of the dispersion hopper 1 and is connected thereto for injecting the flavouring powder into an air circuit including a flexible delivery hose 11 and an electrostatic gun 2. When the flavouring particles arrive at the gun 2, they pass over an electrode 10 so that an electrostatic charge is applied to the particles in a well known way.

The screw feeder 4 is normally linked to the product line so as to have its rotational speed controlled to provide a flow rate suitable to the electrostatic gun 2. This eliminates the need to vary the injector 8 conveying air pressure during operation so as to adjust the supply of flavouring material to the speed of the product line and enables the injector conveying air pressure to be adjusted to optimum pressure to prevent build up of powder in the hopper 1 and to maintain optimum conveying velocities therethrough the delivery hose 11 and the electrostatic gun 2.

The dispersion hopper together with the sieving grid 7 and injector 8 are vibrated by an air fed vibrator 9 so that free flow of the flavouring powder through the sieving grid 7 and through the dispersion hopper 1 and injector 8 is enhanced.

The injector 6 is connected to dual air inputs 12 and 13 through non return valves 14 and 15. The air input 13 provides air a conveying pressure for conveying the flavouring powder to the electrostatic gun 2. The air input 13 provides an intermittent air pulses of higher pressure than the conveying pressure for purging purposes under the control of a cyclic timer (not sown) . Typically, the inlet 13 would be set to provide short air purges through the injector 8, hose 11 and gun 2 at seven to ten second intervals but the frequency and duration of the pulses can be set to any desired rates in dependence on the characteristics of the powder being used.

A modification of the powder flavouring system of figure 1 is shown in figure 2. In this modification, the screw feeder 4 providing outlet from the feed hopper 3 is connected directly into the side wall of the dispersion hopper 1. Because of this direct connection between the feeder 4 and the hopper 1, the hopper 1 is provided with

a flexible bellows portion 16 for insulating the upper part of the dispersion hopper 1, and thus the feeder 4 from vibration of the lower part of the hopper 1.

The dispersion hopper 1 is carried by a support arm 17 by way of a flange 18 connected to the vibrator 9 which is in turn carried by the support 17.

Claims

1. An electrostatic flavouring system comprising a hopper (1) for receiving a flavouring material from a supply (3, 4), an injector (8) connected to the outlet of the hopper (1), an electrostatic spray gun (2) connected via a hose (11) to the injector (8) and two air feed means (12, 13) for feeding air to the injector (8), the first air means (12) providing air at conveying pressure and the second air means (13) providing air at a higher pressure for the purpose of purging the injector (8) and/or the hose (11) and/or the electrostatic gun (2).

2. A system as claimed in claim 1, characterized in that both air feed means (12, 13) feed into a single inlet in the injector (8).

3. A system as claimed in claim 1 or 2, characterized in that one or both of the air feeds means (12, 13) has a non return valve (14, 15).

4. A system as claimed in claim 1, 2 or 3, characterized by a vibrator (9) clamped to the hopper (1).

5. A system as claimed in claim 1, 2 or 3, characterized by a vibrator (9) through which the hopper (1) is connected to a support arm (17).

6. A system as claimed in any preceding claim, characterized in that a screw feeder (4) is arranged to feed the flavouring material into the upper part of the hopper (1).

7. A system as claimed in claim 6, characterized in that the screw feeder (4) is connected directly into the side of the hopper (1).

8. A system as claimed in claim 6 or 7, characterized in that a sieving grid (7) is located in the inlet path of the flavouring material into the hopper (1).

9. A system as claimed in any one of claims 6 to 8, characterized in that control means are provided for adjusting the speed of rotation of the screw feeder in relation to the flavouring material used.

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FIG.1

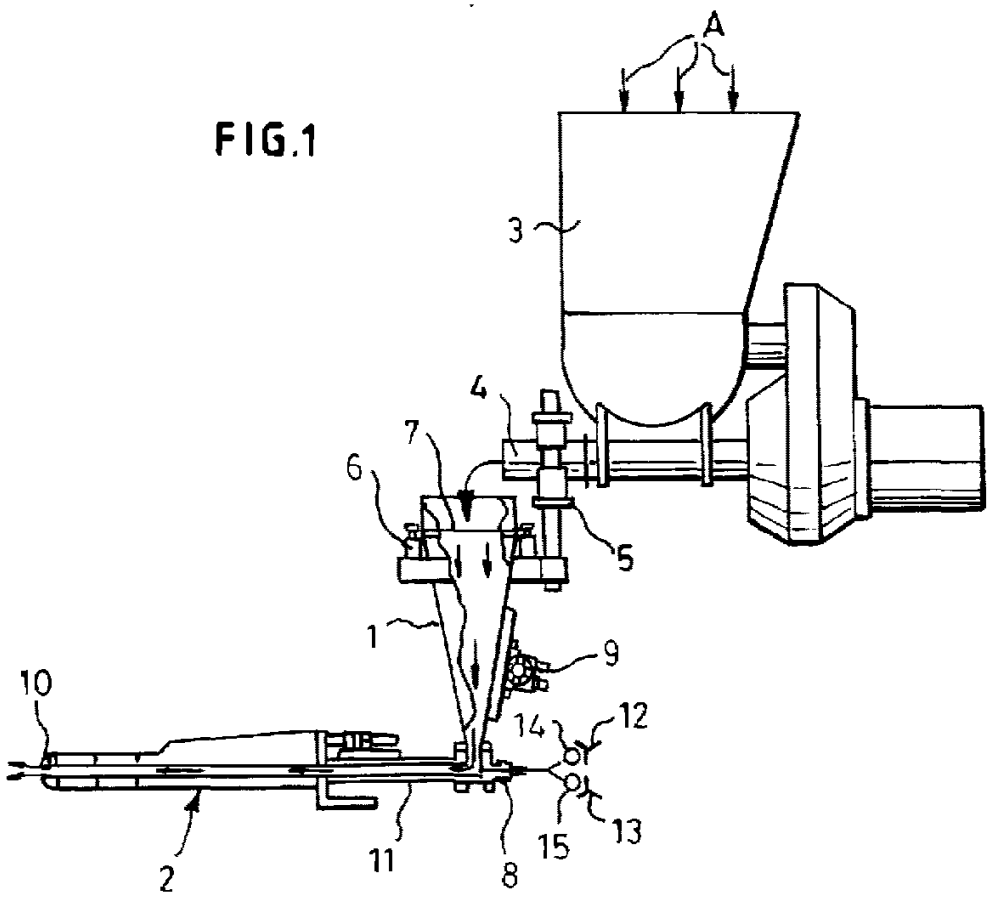
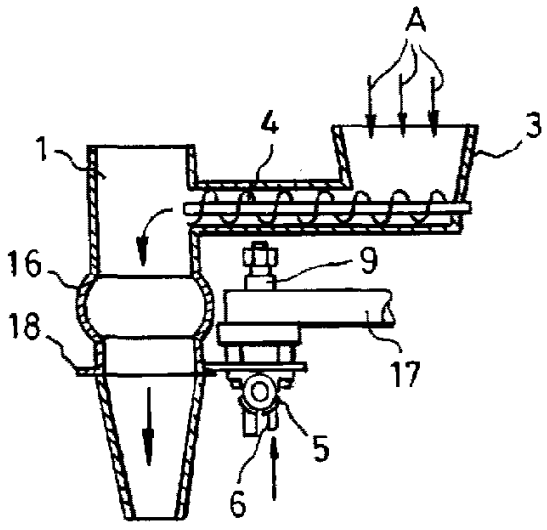


FIG.2



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(54) Encapsulation of active ingredients

(57) A process for preparing free-flowing and during handling dust-free micro-particles, at least 90% by weight having a diameter of 100-400 μm, containing one or more active ingredients in a glassy matrix, using a multi-stage spray drying unit, by forming an aqueous solution which contains on solid basis from 40 to 70 % by weight of at least one low molecular weight carbohydrate and/or polyhydroxy compound and 30-60% by weight of at least one high molecular weight film forming agent, whereby the aqueous solution contains at least 50% by weight of said agent(s); incorporating at least one active ingredient into the solution and building an emulsion or suspension, whereby said emulsion or suspension contains on aqueous basis between 1-35% by weight of the active ingredient(s); spray drying the emulsion or suspension into a spray drying tower at an air inlet temperature of 100-180°C and an air outlet temperature of 60-95°C; transferring to a fluid bed section the resulting surface dried semi-solid micro-particles having a water content of about 10-20% by weight and having a particle size of about 10-200 μm and continuing drying and simultaneously agglomerating said micro-particles at an air temperature of between 25°C and 55°C resulting in solid, free-flowing particles with a glassy matrix having mainly a size of 400 μm or lower and having a water content of about 2-6% by weight; collecting the particles, at least 90% by weight of that particles having a size in the range of 100-400 μm and a water content of 0.5-4% by weight and recycling the particles having a size mainly below about 100 μm from the fluid bed either into the spray dying tower to allow growth of these particles by wetting the particles with fresh sprayed in emulsion or suspension or to the upper part of the fluid bed to allow growth of these particles by agglomeration to a size in the range of 100-400 μm.

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Description

[0001] There exists a demand for encapsulating active ingredients, which are food, feed, beverage or pharmaceutical additives, especially vitamins and more specifically flavors.

[0002] Among them, the need for dry versions of liquid flavors is the most important one. Especially dry versions of liquid flavors are needed for flavoring dry food and beverage products, such as, for example, tea, instant coffee, instant soups and desserts, dry beverage powders, effervescent tablets and pharmaceutical products.

[0003] Several techniques have been developed for producing dry flavors. Among them, the plating on a carrier technique and the spray drying technique are most widely used. These methods are simple and cost saving. However, both techniques have the serious disadvantage of providing no or only limited protection of the flavor against heat, moisture, and oxydation. Hence the appropriate encapsulated flavors have a bad shelf life stability. Therefore, these methods are not suitable for use in combination with flavors sensitive against oxidation such as, for example, citrus flavors.

[0004] In this respect one of the most successful approaches to produce dry flavors and especially to improve the shelf life stability of dry flavors, is their encapsulation in a glassy sugar matrix. The preferred technology for producing glassy encapsulated flavors is extrusion. The products of the extrusion technology are very stable against oxidation and show high retention of volatiles during storage. However, extruded flavors are considerably more expensive than spray dried flavors because of the relatively low flavor load and the need of using a multi-step and multi-component process consisting of at least a heating, an extrusion, a washing (usually with isopropanol), a drying and a grinding step. Moreover, a solvent recovery step has normally to be included as well. Another drawbank of encapsulation of flavors by the extrusion technique is that the flavor is subjected to high temperatures, which might induce decomposition of sensitive flavor constituents. Hence, there exists a need to keep the melt temperature as low as possible. But this limits the choice of carrier materials. Low molecular weight carbohydrates, in combination with plasticizers such as glycerin and water, are used to keep the melt temperature as low as possible. However, a high content of low molecular weight carbohydrates and glycerin increase the hygroscopicity of the resulting powder which, in turn, results in a non-free-flowing, sticky product with high risk of lump formation. Increase of water content is also problematic because of the enhanced flavor losses at the exit of the extruder and/or subsequent drying.

[0005] US Patent No. 3,971,852 describes microparticulate compositions with flavor oil encapsulated in a glassy matrix that consists of a mixture of a polysaccharide with emulsifying properties and low molecular weight polyhydroxy compounds such as sugars or sugar alcohols. Standard spray drying is used to produce spherical particles having a flavor oil contant of up to 80% by volume and an extractable oil of not more than 5%. The stability of the resulting dry flavors is claimed to be better than spray dried flavors prepared according to prior art.

[0006] US Patent 3,314,803 describes a method for encapsulating volatile flavor compounds in a glassy mannitol matrix by spray drying.

[0007] US Patent No. 3,554,768 describes a method for fixing acetaldehyde in selected carbohydrates by drying an aqueous solution of acetaldehyde and selected carbohydrates.

[0008] One of the drawbacks of the above mentioned methods is the high hygroscopicity of the matrix materials. To achieve good stability these products require storage under exclusion of ambient moisture and air. Thus, antioxidants have to be added to prevent oxidation of the flavors fixed in the matrix.

[0009] US Patent No. 4,532,145 describes a spray drying method for encapsulating volatile flavor compounds in a spray dried, moisture-stable matrix consisting of 10-30% low molecular weight carbohydrate such as maltose and at least 70% high molecular weight materials such as maltodextrin. Spray drying is carried out at relatively low temperature, i.e. the inlet temperature ranging from 100 to 180°C and the outlet temperature ranging between 50 and 80°C.

[0010] US Patent No. 5,124,126 describes a method to prepare a moisture and oxygen stable, antioxidant free, fixed flavor having a free flow bulk density of at least 0.5 g/ml and a void space of less than 20% of the spray dried solids, comprising a flavorant encapsulated in a carbohydrate matrix consisting of 22-45% of mono- and disaccharides wherein at least 50% of the mono. and disaccharides is maltose, from 25-50% maltodextrin and from 10-35% high molecular weight film forming carbohydrate. The encapsulated flavor is said to be stable against oxidation for one year at 70° F. The products are obtained at moderate inlet and outlet temperatures of 100-180 and 70-100°C, respectively.

[0011] In all above mentioned spray drying techniques the thermoplastic nature of glassy matrices pose significant processing problems, especially sticking of the thermoplastic particles to the wall of the dryer. Moreover, loss of volatile flavor compounds is still substantial and the resulting powders have relatiely small particle size resulting in dust formation during handling.

[0012] With a multi-stage spray drying method detrimental effects of particle expansion are avoided by spraying at high air temperature to create particles having a semi solid surface in form of a quickly built skin and subsequent continued drying at lower air temperatures in a fluid bed or moving belt dryer. The positive effect of two-stage spray drying on aroma retention has been confirmed experimentally by W.J. Coumans, P.J.A.M. Kerkhof and S. Bruin, Drying Technol. 12 (1 and 2), 99-149 (1994). According to the described process it is not possible to produce particles having high shelf life stability, i.e. having oxygen stability and/or low or no active ingredient diffusing out.

[0013] The French Patent 2,686,486 discloses a method for drying honey using a multistage spray dryer. The advantage of this drying process is said to be the minimum decomposition of sensitive ingredients like vitamins and flavor compounds due to the low temperature during drying. No attempts have been reported to encapsulate flavors.

[0014] The PCT publication WO 91/1782 discloses a method for preparing micro-capsules encapsulating flavorants by multi-stage spray drying. An emulsion, a suspension or a solution of flavorant and matrix material is sprayed into a spraying tower in a cloud of simultaneously introduced fine particles of starch at a 50-120°C. The emulsion drops having freshly solidified surfaces were then transferred to a fluidized bed and maintained fluidized for several hours at 30°C. The particles are more dense and larger than prior art micro-capsules. This characteristic contributes to reduced exposure to oxygen. But a drawback of this process is the long drying time in the fluid bed dryer and the need of introducing of a second carrier or coating. The long resting time in the fluidized bed is here necessary because the already solidified surface of the particles derived from the spray drying hinders the water content inside the particles to migrate out easily, especially to diffuse out of the central part of the particles, thereby also loosing sensitive fragrant materials.

[0015] Although what is said hereafter is related directly to flavors it is clear to a person of skill in the art that it is also valid for other active ingredients. Thus, the invention is not restricted to flavors only but incorporates all active ingredients as they are defined at the beginning.

[0016] From the above description of the prior art it results that there exists a need for a process which overcomes most of the afore mentioned disadvantages or which at least improves an already known process in that the new process is able to produce in a cost saving way micro-capsules containing one or more active ingredients in a glassy matrix which micro-capsules are in the range of 100-400 μm, whereby the micro-capsules shall permit low hygroscopicity and be oxidation stable, i.e. addition of antioxydants shall no more be necessary, and in case of liquid and/or volatile ingredients, especially in case of liquid and/or volatile flavors, at least 85% of their load at the beginning of the process should be kept in the micro-capsules. Further the powder of the micro-capsules should be free flowing and non-dusting and easy dissolvable or distributable in food, feed or beverage, i.e. easy to use. This all is object to the present invention.

[0017] Surprisingly, it has been found that the drawbacks of the prior art spray drying methods for encapsulation in glassy matrices can be reduced or eliminated by the process of the invention, which process using a multi-stage spray drying unit is characterized by the following steps:

a) forming an aqueous solution which contains on solid basis from 40 to 70% by weight of at least one low molecular weight carbohydrate and/or polyhydroxy compound and 30-60% by weight of at least one high molecular weight film forming agent, whereby the aqueous solution contains at least 50% by weight of said agent(s).

b) incorporating at least one active ingredient into the solution of step a) and building an emulsion or suspension, whereby said emulsion or suspension contains on non-aqueous basis between 1-35% by weight of the active ingredient(s).

c) spray drying the emulsion or suspension of step b) into a spray drying tower at an air inlet temperature of 100-180°C and an air outlet temperature of 60-95°C;

d) transferring to a fluid bed section the resulting surface dried semi-solid micro-particles of step c) having a water content of about 10-20% by weight and having a particle size of about 10-200 μm and continuing drying and simultaneously agglomerating said micro-particles at an air temperature of between 25°C and 55°C, especially at about 40-50°C, resulting in solid, free-flowing particles with a glassy matrix having mainly a size of 400 μm or lower and having a water content of about 2-6% by weight;

e) collecting the particles of step d), at least 90% by weight of that particles having a size in the range of 100-400 μm and a water content of 0.5-4% by weight and (simultaneously) recycling the particles having a size mainly below about 100 μm (fines) from the fluid bed either into the spray dying tower to allow growth of these particles by wetting the particles with fresh sprayed in emulsion or suspension of step b) or to the upper part of the fluid bed to allow growth of these particles by agglomeration to a size in the range of 100-400 μm.

[0018] The active ingredient may be a flavor, fragrance and/or vitamin for a food, feed, beverage or pharmaceutical product. Preferably the flavor is selected from the group consisting of a single flavor ingredient, compounded flavor, process flavor, essential oil or extract, whereby the essential oil especially is selected from the group consisting of lime oil, lemon oil, orange oil, peppermint oil, cinnamon, pepper, ginger and mixtures thereof.

[0019] So, the present invention specifically provides a process for the production of flavors encapsulated in a glassy matrix in the form of free-flowing, dust-free powder of micro-capsules, at least 90 % by weight, having a size of about 100-400 μm, which in its properties exceeds the advantages provided by the extruded flavors, which is regarded as the best prior art product, but that can be produced in a continuous process cycle and with higher flavor loads, thus

resulting in significantly lower production costs and costs in use.

[0020] The process of the invention to produce these free-flowing, glassy matrix encapsulated flavors at lower product exposure temperatures than during standard spray drying in order to improve flavor retention reduce thermal decomposition of sensitive flavors and, further, enhance shelf life stability by reducing the matrix porosity resulting from expansion and ballooning that takes place at high drying rates.

[0021] In addition, as the process of the invention for the production of free-flowing, glassy encapsulated flavors of that above mentioned intermediate particle size needs no prolonged drying times and coatings, as, for example, described in the above cited publication WO 91/17821, the production costs are low.

[0022] Further, the process of the invention produces free-flowing glassy particles of low hygroscopicity by reducing the sugar content of the matrix without the need to increase the temperature during the encapsulation process as required with extrusion processes.

[0023] Further details and advantages of the process according to the present invention are described hereafter.

[0024] Surprisingly, by the process according to the present invention it is possible to encapsulate also volatile flavors and/or other active ingredients in a glassy matrix to provide a dense, free flowing powder of 100-400 μm particle size that contains a high level of the volatile encapsulant.

[0025] Generally, the process of the invention comprises the steps of (1) preparing an aqueous solution of the matrix materials, (2) mixing the flavor into the aqueous solution with stirring to form an emulsion or suspension, (3) spraying the emulsion in a spray drying tower under the supply of hot air to create quickly a semi solid skin able for outtake of moisture (water), and (4) subsequently subjecting the resulting particles to continued drying at lower temperatures in a fluid bed.

[0026] The matrix materials consist of low molecular weight water-soluble molecules, and at least one high molecular weight film forming agent. The low molecular weight water-soluble molecules are mono-, di- and oligosaccharides, especially glucose, fructose, maltose, sucrose, lactose, maltodextrin and inulin, or polyhydroxy compounds, especially xylitol, mannitol, sorbitol, lactitol, maltitol and isomalt. The film forming agent material is preferably protein, gum acacia, pectin, modified starch (such as, for example, Capsule E® (octenyl succinated starch, offered by National Starch), or a polyglycerol fatty acid ester, or a mixture thereof.

[0027] If the active ingredient is a water-insoluble liquid, especially a flavor oil, in order to build an emulsion or suspension, the active ingredient is preferably added to the aqueous solution of matrix materials and the mixture is then homogenized until its droplet/particle size is between about 0.2 and 10 μm, preferably about 1-2 μm whereby the emulsion or suspension is preferably adjusted to a viscosity of about 400-1000 cP at 40°C. The amount of the active ingredient, especially of the flavor oil, in the emulsion or suspension is on non-aqueous basis from about 1 to 30 % by weight, preferably from 5 to 25%, more preferably from 10 to 20%.

[0028] In an embodiment of the process of the invention, the liquid drops are specifically dried in two steps:

[0029] In the first step the emulsion which is preferably heated to between 30 and 50°C and sprayed into the spray drying tower in form of fine drops built by means of a rotating disc or a nozzle where they meet a stream of air of a temperature of between 130 and 180°C, more specifically of a temperature of between 145-165°C. As a result, the matrix material in the outer part of the drops solidifies forming particles with a skin that is still permeable for water but no longer permeable for flavorants. The temperature of the hot air is kept high enough that migration of moisture from the inside to the outside may take place within short time but kept low enough to prevent an explosion of steam in the droplets. Otherwise, explosion of steam would increase porosity, and hence, make the matrix permeable also to flavors and oxygen yielding flavor loss, either as liquid or by volatilization and/or oxydation of the flavors. Therefore, the temperature at the outlet of the spray dryer is normally kept at 95°C or below 95°C, specifically in the range of 60-95°C.

[0030] In the second step of the process the powder is fluidized in the internal fluid bed where some agglomeration takes place, which is supported by the residual moisture in the particles which softens the surface when migrating from the inside to the outside of the particles. Residence time in the internal fluid bed is normally about 10 to 30 minutes and depends on the size of the envisaged particle size distribution of the end product. Incoming air at temperature from 25-60°C , specifically at a temperature of about 40-50°C, passing through the fluid bed further dries the particles. Those particles having the envisaged size are seperated or collected, e.g. sieved off, and the fines are recirculated. Thus, particles are continuously dried and removed. The seperated particles have a bulk density of at least 0.4 g/ml and a moisture content of 0.5-4 % by weight.

[0031] The fine particles, mainly below about 100 μm (fines) are preferably collected, by cyclones, or in filters and returned into the spray dryer tower or, alternatively, to the upper part of the fluid bed where they are agglomerated with the other particles thereby enhancing its size to a size in the envisaged range of 100-400 μm. By this way a dust free powder is obtained.

[0032] A method for flavoring a food or beverage product or feed supplement may advantageously be performed by adding the encapsulated flavor in form of micro-particles prepared by the process according to the invention in an effective amount. The micro-particles may be compressed to build bigger units, especially may be compressed into tablets, which in some applications might have an advantage in handling. Preferably the food in this respect is a dry mix of food,

especially an instant soup, sauce or dessert or confectionery, and the beverage product preferably is a dry beverage product, especially a dry beverage powder. More preferably, the dry beverage product is a tea or instant coffee.

[0033] The present invention is described further in the following examples which are presented solely for the non-limiting purpose of further illustrating the invention.

EXAMPLE 1

[0034] An emulsion was prepared from the ingredients listed below:

Ingredient	*Quantity (kg)*
Water	78.49
Potassium hydroxide	0.04
N-Lok	24.91
Maltodextrin	46.74
Santone 8-1-0 (polyglycerol oleic acid ester)	2.13
Sucrose	71.94
Lemon oil	25.75
Total:	250.00

[0035] Water, contained in a jacketed tank, was heated to 50-60°C and potassium hydroxide was added with stirring using a high shear mixer. Then the other ingredients were added one after the other. Addition of the next ingredient was not started before the last one had completely dissolved. Finally, the lemon oil (flavor oil) was added and the mixture was homogenized until the oil droplet size was between 5 and 10 μm. The emulsion temperature was kept at 30-40°C while spray drying. The feed was pumped through a high-pressure homogenizer set at 150 bar in order to further reduce the size of the flavor droplets to about 1 to 2 μm.

[0036] The emulsion was fed to a pressure nozzle installed on a multistage spray dryer Anhydro SPD and sprayed into the spraying tower under the conditions specified below.

Total solids [kg]	171.5
Total solids [%]	63.8
Inlet spray [°C]	130-150
Outlet spray [°C]	70
Inlet internal fluid bed [°C]	40
Inlet external fluid bed [°C]	35 / 25
Spray pressure [bar]	130
Nozzle (type, diameter)	27/1; 660 μm
Time [hrs]	2.15
Powder yield [kg] size: 100-400 μm	166.2
Powder yield [%] size: 100-400 μm	97

[0037] The fines from the cyclone were recycled into the internal fluid bed. Thus a free flowing powder was obtained with the following properties:

Mean particle size(D(v,0.5)): 212 μm

Moisture content: 2.5%

Tap bulk density: 0.71 g/ml

Absolute density as determined by air pycnometer: 1.2817 g/ml

Total flavor content: 13.5%

Surface oil: <0.1%

EXAMPLE 2

[0038] An emulsion was prepared from the ingredients listed below:

Ingredient	*Quantity (kg)*
Water	95.00
Capsul	15.81
Maltodextrin	39.52
Sucrose	76.42
Orange Flavor 74379	23.25
Total:	250.00

[0039] The emulsion was prepared as described in example 1. Water was heated to 50-60°C and the solid ingredients were dissolved in it one after the other. After adding the orange flavor an emulsion was prepared and dried on the multistage spray dryer. The emulsion temperature was kept at 45-50°C while spray drying. The details of the experiment are listed below.

Total solids [kg]	155.0
Total solids [%]	62.0
Inlet spray [°C]	145-165
Outlet spray [°C]	70 - 73
Inlet internal fluid bed [°C]	55
Inlet external fluid bed [°C]	40 / 25
Spray pressure [bar]	100 - 115
Nozzle	27/1; 670 µm
Time [hrs]	2.33
Powder yield [kg] size: 100-400 µm	147
Powder yield [%] size: 100-400 µm	95

[0040] A free flowing powder was obtained with the following properties:

Mean particle size (D(v,0.5)): 142 µm

Moisture content: 3.8%

Tap bulk density: 0.65 g/ml

Absolute density as determined by air pycnometer: 1.2390 g/ml

Total flavor content: 14.0%

Surface oil: <0.1%

[0041] The products of both examples are free flowing and non-dusting powders consisting of particles having a high active ingredient content which particles have a size double that produced according normal tower dryer techniques but yet of that size which makes it easy for its dissolution or distribution in the food, feed, beverage or pharmaceutical end product. The flavor oil recovery is high, namely 88-95%, whereby the so-called surface oil, i.e. the flavor oil persisting on the surface of the particles, is extremely low. The particles have high densities which is indicative for low porosities of the particles. Further, the oxygen uptake in meq/kg flavor oil in encapsulation is very low indicating excellent encapsulation protection from oxygen attack and also from friability.

[0042] The shelf life is about 24 to 36 months. Thus, based on the above analytical results and the specific configuration of the micro particles the shelf life is enhanced tremendously compared with encapsulated flavor particles prepared according methods of the state of the art. The yielded extremely good flavor stability and, hence, the significantly longer shelf life is not known so far for similar products.

[0043] While the invention has been illustrated and described with respect to illustrative embodiments and modes of practice, it will be apparent to those skilled in the art that various modifications and improvements may be made without departing from the scope and spirit of the invention. Accordingly, the invention is not to be limited by the illustrative embodiments and modes of practice.

Claims

1. A process for preparing free-flowing and during handling dust-free micro-particles, at least 90% by weight having a diameter of 100-400 μm, containing one or more active ingredients in a glassy matrix, using a multi-stage spray drying unit comprising the steps of:

   a) forming an aqueous solution which contains on solid basis from 40 to 70 % by weight of at least one low molecular weight carbohydrate and/or polyhydroxy compound and 30-60% by weight of at least one high molecular weight film forming agent, whereby the aqueous solution contains at least 50% by weight of said agent(s).

   b) incorporating at least one active ingredient into the solution of step a) and building an emulsion or suspension, whereby said emulsion or suspension contains on aqueous basis between 1-35% by weight of the active ingredient(s).

   c) spray drying the emulsion or suspension of step b) into a spray drying tower at an air inlet temperature of 100-180°C and an air outlet temperature of 60-95°C;

   d) transferring to a fluid bed section the resulting surface dried semi-solid micro-particles of step c) having a water content of about 10-20% by weight and having a particle size of about 10-200 μm and continuing drying and simultaneously agglomerating said micro-particles at an air temperature of between 25°C and 55°C, especially at about 40-50°C, resulting in solid, free-flowing particles with a glassy matrix having mainly a size of 400 μm or lower and having a water content of about 2-6% by weight;

   e) collecting the particles of step d), at least 90% by weight of that particles having a size in the range of 100-400 μm and a water content of 0.5-4% by weight and recycling the particles having a size mainly below about 100 μm from the fluid bed either into the spray drying tower to allow growth of these particles by wetting the particles with fresh sprayed in emulsion or suspension of step b) or to the upper part of the fluid bed to allow growth of these particles by agglomeration to a size in the range of 100-400 μm;

2. The process of claim 1, wherein the active ingredient is a flavor, fragrance and/or a vitamin for a food, feed, beverage, or pharmaceutical product.

3. The process of claim 2, wherein the flavor is selected from the group consisting of a single flavor ingredient, com-

pounded flavor, process flavor, essential oil or extract.

4. The process of claim 3, wherein the essential oil is selected from the group consisting of lime oil, lemon oil, orange oil, peppermint oil, cinnamon, pepper, ginger and mixtures thereof.

5. The process of any one of the claims 1-4, wherein the low molecular weight carbohydrate is a mono-, di- and oligosaccharide and/or the corresponding alcohol.

6. The process of claim 5, wherein the carbohydrate is selected from the group consisting of glucose, fructose, maltose, sucrose, lactose, maltodextrin and inulin.

7. The process of any one of the claims 1-4, wherein the polyhydroxy compound is selected from the group consisting of xylitol, mannitol, sorbitol, lactitol, maltitol and isomalt.

8. The process of any one of the claims 1-7, wherein the film forming agent is selected from the group consisting of protein, gum acacia, pectin, modified starch and a polyglycerol fatty acid ester.

9. The process of any one of the claims 1-8, wherein said spray drying is performed at an air inlet temperature of about 130-180°C, and an air outlet temperature of about 60-95°C.

10. The process of claim 9, wherein the air inlet temperature is 145-165°C.

11. A dust-free powder of micro-capsules, at least 90% by weight having a particle size of about 100-400 µm, with a bulk density of at least 0.4 g/ml and a moisture content of 0.5-4% by weight having a glassy matrix of at least one mono-, di- and oligosaccharide and/or the corresponding alcohol containing entrapped at least one active ingredient, said particles being formed by spraying an aqueous emulsion or suspension of active ingredient(s) and matrix material into a spray drying tower under the supply of air at a temperature of about 100-180°C, preferably at a temperature of 130-180°C, more preferably at a temperature of 145-165°C, transferring the partly dried particles to a fluid bed for final drying at a temperature of between 25 and 60°C , more preferably at a temperature of about 40-50°C, while recirculating the finer particles from the fluid bed into the spray drying tower to allow particle growth of these particles by wetting the particles with fresh sprayed in emulsion or suspension or to the upper part of the fluid bed to allow the growth of these particles by agglomeration.

12. A method for flavoring a food or beverage product or feed supplement, comprising adding the encapsulated flavor in form of micro-particles prepared by the process according to any one of the claims 1-10 in an effective amount.

13. The method of claim 12, wherein the micro-particles are compressed into tablets.

14. The method of claim 12 or 13, comprising adding the encapsulated flavor to a dry mix of food, especially to an instant soup, sauce or dessert.

15. The method of claim 12, wherein the beverage product is a dry beverage product, especially a dry beverage powder.

16. The method of claim 15, wherein the dry beverage product is tea or instant coffee.

17. The method of claim 12, comprising adding the encapsulated flavor to confectionery.

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- **PATENT ABSTRACTS OF JAPAN vol. 004, no. 135 (C-025), 20. September 1980 (1980-09-20) & JP 55 086501 A (TAKASAGO THERMAL ENG CO LTS), 30. Juni 1980 (1980-06-30)**

Anmerkung: Innerhalb von neun Monaten nach der Bekanntmachung des Hinweises auf die Erteilung des europäischen Patents kann jedermann beim Europäischen Patentamt gegen das erteilte europäische Patent Einspruch einlegen. Der Einspruch ist schriftlich einzureichen und zu begründen. Er gilt erst als eingelegt, wenn die Einspruchsgebühr entrichtet worden ist. (Art. 99(1) Europäisches Patentübereinkommen).

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Beschreibung

[0001] Die vorliegende Erfindung betrifft ein Verfahren zur Sprühtrocknung von lösungsmittelhaltigen Zusammensetzungen.

[0002] Vorrichtungen zur Sprühtrocknung lösungsmittelhaltiger Zusammensetzungen, insbesondere wasserhaltiger Zusammensetzungen, sind aus dem Stand der Technik bekannt.

[0003] Häufig verwendete Vorrichtungen sind beispielsweise Sprühtürme mit Zerstäuberdüsen, die insbesondere bei flüssigen Edukten (Lösungen, Suspensionen oder Schmelzen) zur Bereitstellung eines pulverförmigen Produktes eingesetzt werden. Hierbei wird die Flüssigkeit meist mit Druckdüsen zerstäubt und trocknet dann im Heißgas im Gleich- oder Gegenstrom. Anschließend wird das trockene Produkt durch Zyklone oder Filter abgeschieden. Wird eine Schmelze zerstäubt und im kalten Gas erstarrt, so spricht man von einem Prillturm.

[0004] Weitere bekannte Sprühtrockner sind Scheibentürme. Diese sind - wie auch die Düsentürme - Kurzzeittrockner. Sie verwenden zur Zerstäubung rotierende Scheiben und sind im Vergleich zum Düsenturm von gedrungener Bauform. Der Vorteil der Zerstäuberscheibe ist deren Unempfindlichkeit gegen Verstopfung der "Düsen" und stark veränderliche Flüssigkeitsdurchsätze.

[0005] Bekannt sind außerdem Sprühtrockner mit integriertem Wirbelbett. Durch den Einbau einer Wirbelschicht am Boden des Sprühturms kann das Produkt dort nachgetrocknet und gesichtet werden. Das Trocknungsgas mit dem Feinstaub wird beispielsweise im oberen Teil des Turmes am Turmkopf abgezogen und der Feinstaub nach der Abtrennung in den Turm zurückgeführt. Deshalb können auch vergleichsweise klebrige und langsam trocknende Edukte verarbeitet werden. Als Produkt werden gut dispergierbare Agglomerate erhalten, die größer und damit zumeist staubärmer als die Pulver der Düsen- und Scheibentürme sind.

[0006] Im weiteren Sinne gleichfalls zu den Sprühtrocknern zu zählen sind Wirbelschicht-Sprühgranulatoren ("Agglomerations-Trockner"), die der Herstellung von Granulaten im Bereich von 0.5 mm bis zu mehreren mm aus zerstäubbaren Lösungen, Suspensionen und Schmelzen dienen. Zur Zerstäubung werden Zweistoffdüsen eingesetzt. Das Produkt ist meist abriebfest und hat ein relativ hohes Schüttgewicht. Die Lösegeschwindigkeit ist deshalb, verglichen mit anderen Sprühprodukten, geringer. Ein solcher Granulator kann auch zum Beschichten von Granulaten benutzt werden, dann wird er meist diskontinuierlich betrieben.

[0007] Ein wesentliches Einsatzgebiet von Sprühtrocknern ist die Trocknung wäßriger Zubereitungen von Netz-, Wasch- und Reinigungsmitteln zur Herstellung entsprechender Mittel in schütt- und rieselfähiger Pulverform. Die Mittel werden in Düsen- oder Scheibensprühtürmen in der Regel im Bereich des Umgebungsdrucks in Gleichstrom- oder häufiger in der Gegenstromfahrweise großtechnisch gewonnen. Aus der umfangreichen Fachliteratur sei lediglich beispielhaft verwiesen auf K. Masters "Spray Drying Handbook", Longman Scientific & Technical 1991, ISBN 0-582-06266-7.

[0008] Aus der WO 92/05849 ist ein Verfahren zur Sprühtrocknung von Wertstoffen und Wertstoffgemischen unter Verwendung von überhitztem Wasserdampf bekannt. Der Einsatz überhitzten Wasserdampfes vermeidet oxidative Schädigungen des Trocknungsgutes.

[0009] Aus der WO 96/04973 ist ein Verfahren zur Sprühtrocknung wasserhaltiger Wertstoffzubereitungen aus dem Bereich der Netz-, Wasch- und/oder Reinigungsmittel bekannt, das durch Einbringen eines pulver- oder puderförmigen Hilfsstoffes in den Innenraum der Sprühtrocknungszone Anbackungen an die Innenwand des Trockners vermeidet.

[0010] Die US-A-5,723,433 beschreibt ein Verfahren zum Entfernen von Lösungsmitteln aus einer pastösen Tensidmasse, das umfaßt, die pastöse Masse unter Druck in einen Trocknungskanal einzuführen und am Einlaß des Kanals den Druck so abzusenken, daß es zu einer Entspannungsverdampfung (Flash-Verdampfung) bestimmter Komponenten der pastösen Masse kommt. Die pastöse Masse wird in dem Trockungskanal erhitzt und durch die während der Entspannungsverdampfung freiwerdenden Gase durch den Kanal getrieben. Ergebnis des Verfahrens ist eine konzentrierte Tensidpaste, die am Auslaß des Trocknungskanales erhalten wird.

[0011] Das Patent US 3,450,494 offenbart ein Verfahren zur Herstellung von Natriumsilikat Partikeln, in welchem eine wässrige Natriumsilikat-Dispersion unter Druck erhitzt in eine Expansionszone, in welcher ein niedrigerer Druck herrscht, eingebracht wird. Die Expansionszone in dem offenbarten Verfahren weist Umgebungstemperatur auf; ein Heiß-oder Trocknungsgas wird in die Expansionszone nicht eingeleitet. Da kein Heiß- oder Trocknungsgas eingesetzt wird, kühlen die gebildeten Partikel schnell ab, was zur Ausbildung einer zerklüfteten Partikel-Struktur führt. Die Verfahrensendprodukte des offenbarten Verfahrens unterscheiden sich grundlegend von Granulaten, welche durch Sprühtrocknungsverfahren hergestellt wurden.

[0012] In JP-A-55086501 wird ein Verfahren beschrieben, in welchem ein Slurry unter Druck erhitzt, durch eine Drosselklappe zwecks Absenkung des Drucks geführt und anschließend in einen Trocknungsturm eingesprüht wird. Durch die schnelle Ausdehnung der flüssigen Komponenten und Verdunstung des Wassers werden trockene, feine Partikel gebildet.

[0013] Eine Vakuum-Trocknungsmethode, in welcher ein flüssiges Beschickungsgut zuerst in einen Lösungsmitteldampf und anschließend in einen Vakuumraum eingeführt wird, wird in dem Patent US 5,232,550 offenbart. Bereits im Lösungsmitteldampf bilden sich aus dem flüssigem Beschickungsgut sphärische Partikel, die dann in den Vakuumraum

gelangen und dort mittels Vakuumverdunstung getrocknet werden.

[0014] Die bekannten Verfahren zur Sprühtrocknung flüssiger oder pastöser Zusammensetzungen sind nachteiligerweise durch einen sehr hohen Energieverbrauch gekennzeichnet. Die eingesetzte Energie dient zu einem erheblichen Teil nicht der Lösungsmittelverdampfung, sondern der Deckung von Wärmeverlusten, die beispielsweise durch das warme Abgas entstehen.

[0015] Nachteilig ist außerdem, daß bei der Sprühtrocknung von Zusammensetzungen, die anfällig für mikrobielle Kontaminationen sind, die enthaltenenen Mikroorganismen nicht zuverlässig abgetötet werden, da die Zusammensetzungen im Ansetzbehälter des Sprühtrockners meist nur für kurze Zeit und oft lediglich auf eine Temperatur von unter 100 °C erhitzt werden, um die enthaltenen Wertstoffe zu schonen. Auch wenn in einem sehr heißen Gasstrom getrocknet wird, sind die Partikel dem Heißgas nur Sekunden ausgesetzt, was zur Abtötung vieler unerwünschter Mikroorganismen nicht ausreicht. Problematisch ist diese Keimbelastung insbesondere bei der Herstellung von Pulvern oder Granulaten, die in Le-bensmitteln, Kosmetika oder Arzneimitteln Verwendung finden sollen. Erschwerend kommt hinzu, daß viele Mikroorganismen sich in dem getrockneten Produkt in Abwesenheit von Wasser zwar nicht mehr vermehren; aber auch nicht absterben, sondern extrem widerstandsfähige Dauerformen wie beispielsweise Sporen ausbilden.

[0016] Das getrocknete Produkt ist folglich weder optisch noch olfaktorisch als kontaminiert zu erkennen; wird es jedoch wieder mit Wasser in Kontakt gebracht, beispielsweise in Wasser gelöst, kann es zu erheblichen Keimbelastungen kommen, wenn das Produkt nicht binnen weniger Stunden verbraucht wird.

[0017] Der vorliegenden Erfindung liegt somit die Aufgabe zugrunde, ein Sprühtrocknungsverfahren bereitzustellen, der die obengenannten Nachteile des Standes der Technik vermeidet.

[0018] Diese Aufgabe wird erfindungsgemäß gelöst durch ein Verfahren gemäß Anspruch 10. Eine geeignete Vorrichtung zur Sprühtrocknung lösungsmittelhaltiger Zusammensetzungen, umfaßt:

a) eine Zuführung für eine flüssige oder pastöse lösungsmittelhaltige Zusammensetzung,
b) Mittel zum Erhitzen der flüssigen oder pastösen lösungsmittelhaltigen Zusammensetzung auf eine Temperatur, die über dem Siedepunkt des Lösungsmittels liegt,
c) Mittel zum Transport der in b) erhitzten flüssigen oder pastösen lösungsmittelhaltigen Zusammensetzung unter Überdruck und bei einer Temperatur, die über dem Siedepunkt des Lösungsmittels liegt,
d) Mittel zur Zerstäubung der in b) erhitzten und in c) unter Überdruck transportierten flüssigen oder pastösen lösungsmittelhaltigen Zusammensetzung bei einer Temperatur, die über dem Siedepunkt des Lösungsmittels liegt sowie
e) einen nicht unter Überdruck befindlichen Relaxationsraum, der die mittels d) zerstäubte Zusammensetzung aufnimmt.

[0019] Vorteilhafterweise ist der Energiebedarf des erfindungsgemäßen Verfahrens bei gleicher Trocknungsleistung geringer als der herkömmlicher Sprühtrockner. Die Energieerspamis liegt in der Regel bei etwa 10 % bis etwa 35 %.

[0020] Zudem erfolgt durch den Transport und die Zerstäubung unter Überdruck eine weitgehende Drucksterilisation der zu trocknenden Zusammensetzung, insbesondere wenn die Suspension über 150 °C erhitzt wird.

[0021] Bei der unter Überdruck erfolgenden Zerstäubung in den nicht unter Überdruck befindlichen Relaxationsraum kommt es zu einer Entspannungsverdampfung des Lösungsmittels oder zumindest von Teilen des Lösungsmittels.

[0022] Bei der Entspannungsverdampfung (Flash-Verdampfung) wird ein flüssiger Stoffstrom auf einen niedrigeren Druck gedrosselt. Dabei verdampft ein Teil der Flüssigkeit, die sich dabei abkühlt, d.h. die für den Verdampfungsvorgang erforderliche Verdampfungsenthalpie wird hierbei der verbleibenden Restflüssigkeit entnommen und nicht von außen zugeführt. Im Detail kann man sich den Entspannungsverdampfungsvorgang so vorstellen, daß sich nach der Druckabsenkung in der Flüssigkeit zunächst eine große Anzahl kleinster Dampfblasen bildet. Diese Dampfblasen wachsen dann soweit an, bis bei ausreichender Verweilzeit im Entspannungsbehälter soviel Dampf gebildet wurde wie gerade dem thermodynamischen Gleichgewicht entspricht.

[0023] Der rapide Druckabfall hat eine zusätzliche sterilisierende Wirkung, da er die Zellmembranen und/oder Zellwände noch intakter Mikroorganismen zerreißt und diese dadurch abtötet.

[0024] Ein weiterer, überraschender positiver Effekt, der bei der Anwendung des erfindungsgemäßen Verfahrens zu beobachten ist, besteht in der Erhöhung des sogenannten Berger Weissgrades, bei der Trocknung von Wasch-, Netz- oder Reinigungsmitteln um etwa 20 % bis etwa 70 %, meistens um etwa 50%, verglichen mit konventionell sprühgetrockneten Produkten.

[0025] Eine flüssige oder pastöse lösungsmittelhaltige Zusammensetzung im Sinne der vorliegenden Erfindung kann jede zweckmäßige Lösung, Dispersion oder Kombination von Lösung und Dispersion eines Feststoffs in dem Lösungsmittel sein.

[0026] Als Mittel b) der Vorrichtung kann grundsätzlich jede Wärmequelle eingesetzt werden, die geeignet ist, die flüssige oder pastöse lösungsmittelhaltige Zusammensetzung auf eine Temperatur zu erhitzen, die über dem Siedepunkt des Lösungsmittels liegt. Geeignete Wärmequellen sind beispielsweise Gasbrenner, Heizstrahler oder insbesondere

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Wärmetauscher.

[0027] Die Mittel b) und/oder c) sind vorzugsweise mit einer Mischvorrichtung, insbesondere mit einem üblichen dynamischen oder statischen Mischer, besonders bevorzugt mit einem statischen Mischer, ganz besonders bevorzugt mit einem Doppelmantel-Statikmischer, versehen.

[0028] Als Mittel d) der Vorrichtung eignen sich insbesondere Zerstäuberdüsen, beispielsweise Pneumatik-Zerstäuberdüsen, Hohlkegeldüsen, Vollkegeldüsen, Flachstrahldüsen, Vollstrahldüsen oder Ultraschallzerstäuber.

[0029] Die in den Mitteln b) bis d) herrschende Temperatur hängt von der Beschaffenheit des Lösungsmittels und der lösungsmittelhaltigen Zusammensetzung ab.

[0030] Vorzugsweise ist das Lösungsmittel Wasser. In diesem Fall liegt die Temperatur in den Mitteln b) bis d) über 100 °C, insbesondere im Bereich von 100 °C bis 240 °C, besonders bevorzugt im Bereich von 140 °C bis 160 °C, ganz besonders bevorzugt bei etwa 150 °C.

[0031] Der Überdruck in den Mitteln c) und d) ist ebenfalls von der Beschaffenheit des Lösungsmittels und der lösungsmittelhaltigen Zusammensetzung abhängig. Wird Wasser als Lösungsmittel verwendet, beispielsweise bei Wasch- oder Reinigungsmittel-Slurries, liegt der Überdruck im Bereich von etwa 5 bar bis etwa 60 bar, insbesondere etwa 20 bar bis etwa 50 bar, besonders bevorzugt etwa 30 bar bis etwa 40 bar.

[0032] Im Relaxationsraum e) herrscht Normaldruck. Bevorzugt sind die Merkmale a) bis e) in einen Sprühturm integriert.

[0033] Die die zerstäubte Zusammensetzung wird in einem Strom aus Heißgas, insbesondere in einem Strom aus überhitztem Wasserdampf als Heißgas, geführt, wie in der WO 92/05849 beschrieben, auf die hiermit in vollem Umfang Bezug genommen wird.

[0034] Die Anwendung des erfindungsgemäßen Verfahrens liegt auf dem Gebiet der Herstellung von pulverförmigen, lagerbeständig schütt- und rieselfähigen Textilwaschmitteln oder bei der Gewinnung entsprechender Handelsformen von Wertstoffen aus diesem Bereich, wie Tensiden oder tensidhaltigen Mehrkomponentengemischen.

[0035] Im nachfolgenden finden sich allgemeine Angaben von Wertstoffen für die unmittelbare oder mittelbare Verwendung bei der Herstellung von Netz-, Wasch- und/oder Reinigungsmitteln, wobei diese Zusammenstellung an heute üblichen Komponenten von Textilwaschmitteln dargestellt ist.

[0036] Als anionische Tenside sind zum Beispiel Seifen aus natürlichen oder synthetischen, vorzugsweise gesättigten Fettsäuren brauchbar. Geeignet sind insbesondere aus natürlichen Fettsäuren, zum Beispiel Kokos-, Palmkern- oder Talgfettsäuren, abgeleitete Seifengemische. Bevorzugt sind solche, die zu etwa 50 bis 100% aus gesättigten C_{12-18}-Fettsäureseifen und zu etwa 0 bis 50 % aus Ölsäureseife zusammengesetzt sind. Weiterhin geeignete synthetische anionische Tenside sind solche vom Typ der Sulfonate und Sulfate. Besondere Bedeutung kann dabei die erfindungsgemäße Vorrichtung für entsprechende Verbindungen pflanzlichen und/oder tierischen Ursprungs haben.

[0037] Als Tenside vom Sulfonattyp kommen Alkylbenzolsulfonate (C_{9-15}-Alkyl), Olefinsulfonate, d.h. Gemische aus Alken- und Hydroxyalkansulfonaten sowie Sulfonate in Betracht, wie man sie beispielsweise aus C_{12-18}-Monoolefinen mit end- oder innenständiger Doppelbindung durch Sulfonieren mit gasförmigem Schwefeltrioxid und anschließende alkalische oder saure Hydrolyse der Sulfonierungsprodukte erhält. Geeignet sind auch die Alkansulfonate, die aus C_{12-18}-Alkanen durch Sulfochlorierung oder Sulfoxidation und anschließende Hydrolyse beziehungsweise Neutralisation beziehungsweise durch Bisulfitaddition an Olefine erhältlich sind, sowie insbesondere die Ester von Alpha-Sulfofettsäuren (Estersulfonate), zum Beispiel die Alpha-sulfonierten Methylester der hydrierten Kokos-, Palmkern- oder Talgfettsäuren.

[0038] Wichtige Tensid- beziehungsweise Emulgatorkomponenten sind in diesem Zusammenhang auch die sogenannten Di-salze, die sich durch Verseifung der zuvor genannten Alpha-sulfonierten Fettsäure-Methylester beziehungsweise durch unmittelbare Sulfonierung von insbesondere gesättigten Fettsäuren - insbesondere C_{12-18}-Fettsäuren - herstellen lassen. Das erfindungsgemäße Verfahren schafft damit die Möglichkeit, großtechnisch problemfrei Tenside der hier und im nachfolgenden beschriebenen Art auf Naturstoffbasis in trokkener rieselfähiger Konzentratform zur Verfügung zu stellen, die praktisch unbegrenzte Lagerbeständigkeit beinhaltet und damit einen wesentlichen Beitrag zum weltweit angestrebten ABS-Austausch leisten zu können.

[0039] Geeignete Tenside vom Sulfattyp sind die Schwefelsäuremonoester aus primären Alkoholen natürlichen und synthetischen Ursprungs, das heißt aus Fettalkoholen, zum Beispiel Kokosfettalkoholen, Talgfettalkoholen, Oleylalkohol, Lauryl-, Myristyl-, Palmityl- oder Stearylalkohol, oder den C_{10-20}-Oxoalkoholen, und diejenigen sekundärer Alkohole dieser Kettenlänge.

[0040] Auch die Schwefelsäuremonoester der mit insbesondere 1 bis 6 Mol Ethylenoxid ethoxylierten Alkohole natürlichen und/oder synthetischen Ursprungs sind geeignete Komponenten. Als Beispiel für Synthese-Alkohole seien Verbindungen wie 2-Methyl-verzweigte C_{9-11}-Alkohole mit im Durchschnitt 3,5 Mol Ethylenoxid genannt. Ferner eignen sich sulfatierte Fettsäuremonoglyceride. Die anionischen Tenside können in Form ihrer Natrium-, Kalium- und Ammoniumsalze sowie als lösliche Salze organischer Basen vorliegen.

[0041] Als nichtionische Tenside sind Anlagerungsprodukte von 1 bis 40, vorzugsweise 2 bis 20 Mol Ethylenoxid an 1 Mol einer aliphatischen Verbindung mit im wesentlichen 10 bis 20 Kohlenstoffatomen aus der Gruppe der Alkohole,

Carbonsäuren, Fettamine, Carbonsäureamide oder Alkansulfonamide verwendbar.

[0042] Besonders wichtig sind die Anlagerungsprodukte von 8 bis 20 Mol Ethylenoxid an primäre Alkohole, wie zum Beispiel an Kokos- oder Talgfettalkohole, an Oleylalkohol, an Oxoalkohole, oder an sekundäre Alkohole mit 8 bis 18, vorzugsweise 12 bis 18 C-Atomen. Neben den wasserlöslichen Nonionics sind aber auch nicht beziehungsweise nicht vollständig wasserlösliche Polyglykolether mit 2 bis 7 Ethylenglykolether-Resten im Molekül von Interesse, insbesondere wenn sie zusammen mit wasserlöslichen, nichtionischen oder anionischen Tensiden eingesetzt werden.

[0043] Außerdem können als nichtionische Tenside auch Alkyglykoside der allgemeinen Formel $R\text{-}O\text{-}(G)_x$ eingesetzt werden, in der R einen primären geradkettigen oder verzweigten aliphatischen Rest mit 8 bis 22, vorzugsweise 12 bis 18 C-Atomen bedeutet, G ein Symbol ist, das für eine Glykose-Einheit mit 5 oder 6 C-Atomen steht, und der Oligomerisierungsgrad x zwischen 1 und 10 liegt.

[0044] Als organische und anorganische Gerüst- beziehungsweise Builder-Substanzen eignen sich schwach sauer, neutral oder alkalisch reagierende lösliche und/oder unlösliche Komponenten, die Calciumionen auszufällen oder komplex zu binden vermögen. Geeignete und insbesondere ökologisch unbedenkliche Builder-Substanzen sind Zeolithe.

[0045] Als Zeolith geeignet ist beispielsweise feinkristalliner, synthetischer und gebundenes Wasser enthaltender Zeolith, wie Zeolith A, Zeolith P und Mischungen aus A und P. Als im Handel erhältlicher Zeolith P ist beispielsweise Zeolith MAP® (Handelsprodukt der Firma Crosfield) zu nennen.

[0046] Als weitere besonders geeignete Zeolithe sind Zeolithe vom Faujasit-Typ zu nennen. Zusammen mit den Zeolithen X und Y gehört das Mineral Faujasit zu den Faujasit-Typen innerhalb der Zeolith-Strukturgruppe 4, die durch die Doppelsechsring-Untereinheit D6R gekennzeichnet sind (Vergleiche Donald W. Breck: "Zeolite Molecular Sieves", John Wiley & Sons, New York, London, Sydney, Toronto, 1974, Seite 92). Zur Zeolith-Strukturgruppe 4 zählen neben den genannten Faujasit-Typen noch die Mineralien Chabazit und Gmelinit sowie die synthetischen Zeolithe R (Chabazit-Typ), S (Gmelinit-Typ), L und ZK-5. Die beiden letztgenannten synthetischen Zeolithe haben keine mineralischen Analoga.

[0047] Zeolithe vom Faujasit-Typ sind aus β-Käfigen aufgebaut, die tetrahedral über D6R-Untereinheiten verknüpft sind, wobei die β-Käfige ähnlich den Kohlenstoffatomen im Diamanten angeordnet sind. Das dreidimensionale Netzwerk der erfindungsgemäß geeigneten Zeolithe vom Faujasit-Typ weist Poren von 2,2 und 7,4 Å auf, die Elementarzelle enthält darüber hinaus 8 Kavitäten mit ca. 13 Å Durchmesser und läßt sich durch die Formel $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\ H_2O$ beschreiben. Das Netzwerk des Zeolith X enthält dabei ein Hohlraumvolumen von ungefähr 50%, bezogen auf den dehydratisierten Kristall, was den größten Leerraum aller bekannten Zeolithe darstellt (Zeolith Y: ca. 48% Hohlraumvolumen, Faujasit: ca. 47% Hohlraumvolumen). (Alle Daten aus: Donald W. Breck: "Zeolite Molecular Sieves", John Wiley & Sons, New York, London, Sydney, Toronto, 1974, Seiten 145, 176, 177).

[0048] Im Rahmen der vorliegenden Erfindung kennzeichnet der Begriff "Zeolith vom Faujasit-Typ" alle drei Zeolithe, die die Faujasit-Untergruppe der Zeolith-Strukturgruppe 4 bilden. Neben dem Zeolith X sind erfindungsgemäß also auch Zeolith Y und Faujasit sowie Mischungen dieser Verbindungen geeignet, wobei der reine Zeolith X bevorzugt ist. Auch Mischungen oder Cokristallisate von Zeolithen des Faujasit-Typs mit anderen Zeolithen, die nicht zwingend der Zeolith-Strukturgruppe 4 angehören müssen, sind erfindungsgemäß geeignet, wobei vorzugsweise mindestens 50 Gew.-% der Zeolithe Zeolithe vom Faujasit-Typ sind.

[0049] Die geeigneten Aluminiumsilikate sind kommerziell erhältlich, und die Methoden zu ihrer Darstellung sind in Standardmonographien beschrieben.

[0050] Beispiele für kommerziell erhältliche Zeolithe vom X-Typ können durch die folgenden Formeln beschrieben werden:

$$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot x\ H_2O,$$

$$K_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot x\ H_2O,$$

$$Ca_{40}Na_6[(AlO_2)_{86}(SiO_2)_{106}] \cdot x\ H_2O,$$

$$Sr_{21}Ba_{22}[(AlO_2)_{86}(SiO_2)_{106}] \cdot x\ H_2O,$$

in denen x Werte zwischen 0 und 276 annehmen kann. Diese Zeolithe weisen Porengrößen von 8,0 bis 8,4 Å auf.

[0051] Geeignet ist beispielsweise auch der in der europäischen Patentanmeldung EP-A-816 291 beschriebene Zeolith A-LSX, der einem Co-Kristallisat aus Zeolith X und Zeolith A entspricht und in seiner wasserfreien Form die Formel $(M_{2/n}O + M'_{2/n}O) \cdot Al_2O_3 \cdot zSiO_2$ besitzt, wobei M und M' Alkali- oder Erdalkalimetalle sein können und z eine Zahl zwischen 2,1 und 2,6 ist. Kommerziell erhältlich ist dieses Produkt unter dem Markennamen VEGOBOND AX von der Firma CONDEA Augusta S.p.A.

[0052] Auch Zeolithe vom Y-Typ sind kommerziell erhältlich und lassen sich beispielsweise durch die Formeln

$Na_{56}[(AlO_2)_{56}(SiO_2)]_{136}] \cdot x\ H_2O$,

$K_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot x\ H_2O$,

in denen x für Zahlen zwischen 0 und 276 steht, beschreiben. Diese Zeolithe weisen Porengrößen von 8,0 Å auf.

[0053] Die Teilchengrößen der geeigneten Zeolithe vom Faujasit-Typ liegt dabei im Bereich von 0,1 bis zu 100 µm, vorzugsweise zwischen 0,5 und 50 µm und insbesondere zwischen 1 und 30 µm, jeweils mit Standard-Teilchengrößenbestimmungsmethoden gemessen.

[0054] Als weitere Builder-Bestandteile, die insbesondere zusamen mit den Zeolithen eingesetzt werden können, kommen (co-)polymere Polycarboxylate in Betracht, wie Polyacrylate, Polymethacrylate und insbesondere Copolymere der Acrylsäure mit Maleinsäure, vorzugsweise solche mit 50 % bis 10 % Maleinsäure. Das Molekulargewicht der Homopolymeren liegt im allgemeinen zwischen 1.000 und 100.000, das der Copolymeren zwischen 2.000 und 200.000, vorzugsweise 50.000 bis 120.000, bezogen auf freie Säure. Ein besonders bevorzugtes Acrylsäure-Maleinsäure-Copolymer weist ein Molekulargewicht von 50.000 bis 100.000 auf.

[0055] Geeignete weitere Verbindungen dieser Klasse sind Copolymere der Acrylsäure oder Methacrylsäure mit Vinylethern, wie Vinylmethylether, in denen der Anteil der Säure mindestens 50% beträgt. Brauchbar sind ferner Polyacetalcarbonsäuren, wie sie beispielsweise in den US-Patentschriften 4,144,226 und 4,146,495 beschrieben sind sowie polymere Säuren, die durch Polymerisation von Acrolein und anschließende Disproportionierung mittels Alkalien erhalten werden und aus Acrylsäureeinheiten und Vinylalkoholeinheiten beziehungsweise Acroleineinheiten aufgebaut sind.

[0056] Brauchbare organische Gerüstsubstanzen sind beispielsweise die bevorzugt in Form ihrer Natriumsalze eingesetzten Polycarbonsäuren, wie Citronensäure und Nitrilotriacetat (NTA), sofern ein derartiger Einsatz aus ökologischen Gründen nicht zu beanstanden ist.

In Fällen, in denen ein Phosphat-Gehalt toleriert wird, können auch Phosphate mitverwendet werden, insbesondere Pentanatriumtriphosphat, gegebenenfalls auch Pyrophosphate sowie Orthophosphate, die in erster Linie als Fällungsmittel für Kalksalze wirken.

[0057] Geeignete anorganische, nicht komplexbildende Salze sind die auch als "Waschalkalien" bezeichneten Bicarbonate, Carbonate, Borate oder Silikate der Alkalien; von den Alkalisilikaten sind vor allem die Natriumsilikate mit einem Verhältnis $Na_2O : SiO_2$ wie 1 : 1 bis 1:3,5 brauchbar.

[0058] Aus den restlichen Gruppen üblicher Waschmittelbestandteile kommen zur Mitverwendung bei der Sprühtrocknung mittels der erfindungsgemäßen Vorrichtung insbesondere Komponenten aus den Klassen der Vergrauungsinhibitoren (Schmutzträger), der Neutralsalze und der textilweichmachenden Hilfsmittel in Betracht.

[0059] Geeignete Vergrauungsinhibitoren sind beispielsweise Carboxymethylcellulose, Methylhydroxyethylcellulose und deren Gemische.

[0060] Als typisches Beispiel für einen geeigneten Vertreter der Neutralsalze ist das bereits erwähnte Natriumsulfat zu nennen.

[0061] Geeignete Weichmacher sind beispielsweise quellfähige Schichtsilikate von der Art entsprechender Montmorillonite, beispielsweise Bentonit.

[0062] Hochtemperatur-sensitive übliche Mischungsbestandteile von Wasch- und Reinigungsmitteln, wie Bleichmittel auf Basis von Per-Verbindungen, Enzyme aus der Klasse Proteasen, Lipasen und Amylasen; beziehungsweise Bakterienstämme oder Pilze, Stabilisatoren, Parfüme, temperaturempfindliche Farbstoffe und dergleichen, werden zweckmäßigerweise mit den zuvor getrockneten Zusammensetzungen vermischt.

Patentansprüche

1. Verfahren zur Herstellung von pulverförmigen oder granulären Wasch-, Netz- oder Reinigungsmitteln bzw. von Rohstoffen für Wasch-, Netz- oder Reinigungsmittel durch Sprühtrocknung von lösungsmittelhaltigen, tensidhaltigen Mehrkomponentengemischen, wobei man

   a) ein flüssiges oder pastöses lösungsmittelhaltiges, tensidhaltiges Mehrkomponentengemisch auf eine Temperatur erhitzt, die über dem Siedepunkt des Lösungsmittels liegt,

   b) das erhitzte flüssige oder pastöse lösungsmittelhaltige, tensidhaltige Mehrkomponentengemisch unter Überdruck und bei einer Temperatur, die über dem Siedepunkt des Lösungsmittels liegt, einer Zerstäubungsvorrichtung zuführt und

   c) das erhitzte flüssige oder pastöse lösungsmittelhaltige, tensidhaltige Mehrkomponentengemisch unter Überdruck und bei einer Temperatur, die über dem Siedepunkt des Lösungsmittels liegt, mittels der Zerstäubungsvorrichtung in einen Relaxationsraum in welchem Normaldruck herrscht, zerstaubt, wobei die zerstäubte Zusammensetzung in einem Strom aus Heißgas geführt wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** das zu entfernende Lösungsmittel Wasser ist.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** das zerstäubte Mehrkomponentengemisch in einem Strom aus überhitztem Wasserdampf geführt wird.

Claims

1. A process for the production of powder-form or granular laundry detergents, wetting agents or cleaners or of raw materials for laundry detergents, wetting agents or cleaners by spray drying of solvent- and surfactant-containing multicomponent mixtures,

   a) a liquid or paste-form solvent- and surfactant-containing multicomponent mixture being heated to a temperature above the boiling point of the solvent,
   b) the heated liquid or paste-form solvent- and surtactant-containing multicomponent mixture being delivered to an atomizer under excess pressure and at a temperature above the boiling point of the solvent and
   c) the heated liquid or paste-form solvent- and surfactant-containing multicomponent mixture being sprayed by the atomizer into a relaxation space where normal pressure prevails under excess pressure and at a temperature above the boiling point of the solvent, the sprayed composition being carried in a stream of hot gas.

2. A process as claimed in claim 1, **characterized in that** the solvent to be removed is water.

3. A process as claimed in claim 1 or 2, **characterized in that** the sprayed multicomponent mixture is carried in a stream of superheated steam.

Revendications

1. Procédé de préparation d'agents de lavage, mouillants ou de nettoyage ou de matières premières pour des agents de lavage, mouillants ou de nettoyage, sous forme de poudre ou de granules, par séchage par pulvérisation de mélanges à plusieurs composants contenant au moins un solvant, contenant au moins un agent tensioactif, dans lequel

   a) on chauffe un mélange à plusieurs composants, liquide ou pâteux, contenant au moins un solvant, contenant au moins un agent tensioactif à une température qui est supérieure au point d'ébullition du solvant,
   b) on introduit le mélange à plusieurs composants, liquide ou pâteux, contenant au moins un solvant, contenant au moins un agent tensioactif chauffé avec une surpression et à une température qui est supérieure au point d'ébullition du solvant, dans un dispositif de pulvérisation et
   c) on pulvérise le mélange à plusieurs composants, liquide ou pâteux, contenant au moins un solvant, contenant au moins un agent tensioactif chauffé avec une surpression et à une température qui est supérieure au point d'ébullition du solvant, au moyen du dispositif de pulvérisation dans une chambre de relaxation dans laquelle régne une pression normale, la composition pulvérisée étant guidée dans un flux de gaz chaud.

2. Procédé selon la revendication 1, **caractérisé en ce que** le solvant à éliminer est de l'eau.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** le mélange à plusieurs composants est guidé dans un flux de vapeur d'eau surchauffée.

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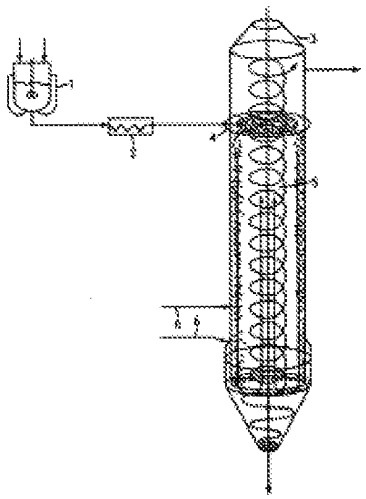
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EP1280591A1 2003-02-05 DEVICE FOR SPRAY-DRYING SOLVENT-CONTAINING COMPOSITIONS (en)



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English Abstract:

The invention relates to a device for spray-drying solvent-containing compositions, to a method for spray-drying solvent-containing compositions, and to the uses of the inventive device and of the inventive method, especially for producing powder washing and cleaning agents.

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(54) SPRAY-DRIED COMPOSITIONS AND METHOD FOR THEIR PREPARATION

SPRÜHGETROCKNETE ZUBEREITUNGEN UND VERFAHREN FÜR DEREN HERSTELLUNG

COMPOSITIONS SECHEES PAR PULVERISATION ET PROCEDE SERVANT A LEUR PREPARATION

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EP 1 435 797 B1

Description

Technical field

[0001] The present invention relates to compositions in an encapsulated form and to a method for the preparation of said compositions.

[0002] An encapsulation is a process by which one or more active ingredients are coated with, or entrapped within, another material or system. In the flavor industry, the encapsulation of flavor ingredients serves to retain the aroma in a food product during storage, protects the flavor from undesirable interactions with the food, minimizes flavor/flavor interactions, guards against either light induced reactions or oxidation, and provides a controlled release of the flavor.

[0003] In this industry, the most common processes for producing encapsulated products are spray-drying and, to a lesser extent, extrusion and coacervation.

Background Art

[0004] Spray-drying is a well-known useful technique to stabilize flavors by encapsulating them in a solid form, suited to many applications.

[0005] In spray-dried powders, an active ingredient such as a flavor or a fragrance, usually hydrophobic, is entrapped as liquid droplets in a solidified matrix of a dehydrated carrier, generally consisting of carbohydrates, such as starches, hydrolyzed starches (maltodextrin), chemically modified starches, emulsifying polymers (gum arabic) and in certain instances monomers and dimers of simple aldohexoses, or any combination thereof. Conventional spray-drying techniques are perfectly well documented in the prior art. See for example Spray-Drying Handbook, 4th ed., K. Masters, (1985) or other reference books on the subject-matter.

[0006] The method for the preparation of a spray-dried powder typically first comprises dispersing a carrier in water, and then mixing this dispersion with a flavor before homogenizing to form an oil-in-water emulsion. The emulsion is then spray-dried to produce a powdered flavor.

[0007] Flavors are traditionally spray-dried in water-soluble carbohydrate matrices. As these matrices dissolve in water readily, the most common applications of the corresponding powdered flavors are dry beverage formulations. However, other applications in the flavor industry as well as in other fields such as the perfumery or the pharmaceutical domains require spray-dried products having a behavior in an aqueous environment different from traditional spray-dried powders. In particular, powders which are able to dissolve in water more slowly than most spray-dried products available today and which may even require a mechanical trigger for the release of the active ingredient encapsulated in the matrix, could be very useful for many applications.

[0008] Means to improve the dispersion of typical spray-dried powders have already been described in the prior art. Agglomeration constitutes such a means and finds applications for instance in instant coffee. However, this process does not suit all applications.

[0009] Now, we have been able to establish that a particular ingredient can be added to the carrier constituting the matrix of a spray-dried product, and, in combination with a wall-forming carbohydrate material, surprisingly improve the behavior of the powder in an aqueous or highly moist environment. This ingredient is agar agar.

[0010] Agar agar is a hydrocolloid, the physical properties of which are well known in the art. More particularly, it has a widespread use in foods as a stabilizer, thickener, humectant and surface finisher.

[0011] Some patent literature discloses the spray-drying of agar itself to provide it in a solid form. On the other hand, agar is often cited as part of the list of encompassing materials susceptible of constituting carriers in an encapsulation system. As an example, one can cite WO 98/33394 which discloses the mixture of a bulking agent with a hydrocolloid in the form of a solid powder which is used as a stabilizing agent in a wide variety of products. Agar Agar has also been disclosed in US 3205175 and GB 911483 as part of a list of materials that can be used in coacervation processes. However, no document from the prior art has ever pointed out or even suggested the possibility of using agar in a spray-dried composition for a specific purpose, when used in defined amounts and in combination with a carbohydrate material.

[0012] For instance, in US 5 124 162 volatile substances are fixed in an amorphous substrate which contains film-forming carbohydrates, without any mention of agar agar . In EP 1 106 081 high levels of film-forming carbohydrates are required, namely 45-70% of the matrix, to be compared with 1-30% as required by the present invention.

[0013] Yet, we have now been able to establish that, in combination with the main carrier material, namely a carbohydrate, and when used in specific amounts, agar agar is an advantageous co-carrier material for a composition intended to be spray-dried. In an unexpected manner, this novel composition proved to be responsible for a complete change in the product's behavior, in an aqueous or highly moist environment, and as regards the release characteristics of the active ingredient there-encapsulated, compared with conventional spray-dried powders.

Disclosure of Invention

[0014] One object of the invention is thus a novel spray-dried composition, comprising one or more active ingredients dispersed in a carrier which comprises at least one wall-forming carbohydrate material and from 1 to 30% by weight of agar agar, relative to the dried weight of the composition.

[0015] What is meant here by "active ingredient", is a liquid ingredient, preferably hydrophobic, which is sought to be protected by way of solid encapsulation. It may include volatile perfuming or flavoring ingredients, as well as other kinds of ingredients such as pharmaceutical actives for instance.

[0016] The system of the invention presents many advantages. While a typical spray-dried product dissolves instantly in water, the composition according to the present invention behaves in a totally different manner in such a medium and makes it possible to provide a controlled release of the encapsulated active ingredient.

[0017] A second object of the present invention is a method for the preparation of such a spray-dried composition, and a further object, its use for the flavoring or perfuming of consumer products such as foods, beverages, or perfuming compositions.

[0018] Finally, the spray-dried powder of the invention can also be advantageously used as an intermediate product or starting product for a double-encapsulation method, i.e. as a solid product susceptible of being subjected to a further encapsulation such as an extrusion in a glassy matrix to provide a granular delivery system, or to a second spray-drying operation in a distinct or similar matrix.

[0019] More objects, aspects and advantages of the invention will become apparent from the detailed description hereafter.

[0020] The present invention thus concerns a composition in the form of a spray-dried powder, comprising one or more active ingredients dispersed in a carrier, wherein said carrier comprises at least one wall-forming carbohydrate material and from 1 to 30% of agar agar, relative to the dried weight of the composition. In another embodiment, the proportion of agar agar in the composition can be limited to 1 to 20%, or even to 1 to 15% by weight, relative to the dried weight of the composition.

[0021] The spray-dried product of the invention turned out to be very useful in particular in an aqueous environment, where it provides a release of the active ingredient which is quite distinct from typical systems known in the prior art. More particularly, the addition of a certain amount of agar agar in the carrier matrix, in combination with a wall-forming carbohydrate material, proved to provide a structure which swells almost instantly upon hydration and forms a gel, wherein the mobility of the active ingredient, in the form of oil droplets, is restricted. As a consequence, even when excess water is present, the gel containing the oil droplets remains intact. Therefore, if the hydrated powder particles are left undisturbed, i.e. are not subjected to constant shear at room temperature, they can retain their integrity for at least 2 weeks, after which the release of the oil from the hydrated particles, when deformed under pressure, is observable. Thus, while typical spray-dried products dissolve instantaneously in an aqueous environment, providing an instant release of the encapsulated active ingredient, the system of the invention provides a controlled release of the active substance. Under another kind of trigger such as shear force or heat, the active substance will be released from the dry powder.

[0022] The spray-dried powder of the invention also presents a particularly advantageous stability in a medium of high relative humidity. Therefore, contrary to powders known up to date, the delivery system of the invention can be stored or be subjected to transportation while protecting in an effective way the active ingredient there-encapsulated.

[0023] The carrier of the spray-dried composition comprises at least one wall-forming carbohydrate material and from 1 to 30% of agar agar which may be in a partially hydrated form. This combination is responsible for the technical effect here-above described.

[0024] Suitable wall-forming carbohydrate materials are substrates such as polyvinyl acetate, polyvinyl alcohol, dextrines, natural or modified starch, pectins, xanthanes, alginates, or yet cellulose derivatives such as for example carboxymethyl cellulose, methyl cellulose or hydroxyethylcellulose. In one particular embodiment of the invention, the carbohydrate material is selected from the group consisting of a maltodextrin, a corn syrup, a chemically modified starch, a hydrogenated starch hydrolysate and a succinylated or hydrolyzed starch.

[0025] The composition of the invention typically comprises from 70 to 99% by weight, relative to the dried weight of the composition, of wall-forming carbohydrate material. Preferably, it contains from 40 to 80% of carbohydrate material.

[0026] In a preferred embodiment, the matrix composition further comprises a plasticizer such as a sugar or sugar derivative, such as sucrose, glucose, lactose, levulose, fructose, maltose, ribose, dextrose, isomalt, sorbitol, mannitol, xylitol, lactitol, maltitol, pentatol, arabinose, pentose, xylose, galactose. Typically, the compositions of the invention may comprise from 0.01 to 50% by weight, relative to the weight of the dried product, of plasticizer.

[0027] An agar agar matrix, futher comprising maltodextrin in admixture with one of the sugars mentioned above, in particular sucrose, is particularly appreciated.

[0028] In addition to carbohydrates and plasticizers, the composition of the invention may comprise an emulsifier intended to promote a homogeneous mix of the oil in the carbohydrate based mixture before spray-drying. The nature and proper amount of the emulsifier can be critically assessed by the process operator without undue experimentation.

Typically, proportions from 1 to 30% by weight, relative to the dried weight of the composition, can be used.

[0029] Many suitable emulsifiers are known in the commerce. Typical examples include soya lecithin, Capsul® (modified maize starch from National Starch), citric acid esters of fatty acids and emulsifying polymers such as gum arabic, but other suitable emulsifiers are cited in reference texts such as Food Emulsifiers and their Applications, 1997, edited by G.L. Hasenhuettl and R.W. Hartel, USA.

[0030] Finally, the composition of the invention, which is initially in the form of an aqueous emulsion, contains, before being spray-dried, from 50 to 90% of water, preferably from 60 to 85% by weight of water, relative to the total weight of the emulsion.

[0031] The active ingredient dispersed in the carrier of the spray-dried composition of the invention will preferably be a hydrophobic flavor or fragrance ingredient or composition of current use. However, the polarity or aqueous solubility of the active ingredient may be chosen as a function of the desired retardation of the release for a given application. In fact, more hydrophilic components will be released faster, as they are able to partition in the outer aqueous phase.

[0032] The terms "flavor and fragrance ingredient or composition" as used herein are deemed to define a variety of flavor and fragrance materials of both natural and synthetic origin. They include single compounds and mixtures. The composition of the invention can encapsulate volatile or labile components in liquid form, preferably hydrophobic. Specific examples of such components may be found in the current literature, e.g. in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M.B. Jacobs, edited by Van Nostrand ; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavoring, and/or aromatizing consumer products, i.e. of imparting an odor and/or a flavor or taste to a consumer product traditionally perfumed or flavored, or of modifying the odor and/or taste of said consumer product.

[0033] Natural extracts can also be encapsulated into the system of the invention ; these include e.g. citrus extracts such as lemon, orange, lime, grapefruit or mandarin oils, or coffee, tea, mint, cocoa, vanilla or essential oils of herbs and spices, amongst other.

[0034] The proportions of active ingredient in the composition are comprised between 0.1 to 60% by weight, relative to the dried weight of the composition. In a particular embodiment, the proportion of the active ingredient is comprised between 20 and 50%.

[0035] Another object of the invention is a method for the preparation of a spray-dried powder, which comprises the steps of emulsifying the active ingredient with an aqueous solution of the matrix carrier comprising at least one wall-forming carbohydrate material and from 1 to 30%, or from 1 to 20% or even from 1 to 15% of agar agar ; homogenizing the emulsion and spray drying the latter to form a particulate product.

[0036] One particular advantage of the process according to the invention lies in the fact that the compositions comprising a combination of agar agar with a carbohydrate, as here-described, demonstrate a retention of the active ingredient (oil) which is advantageously not affected by a variation in the solid content of the starting aqueous emulsion. More particularly, in classical spray-drying processes, a high dilution rate, useful to provide monodispersity of the powder, must be balanced with the fact that the higher is the dilution rate, the lower will be the flavor retention. It is furthermore established that 10% lower solid content in the initial aqueous emulsion should result in noticeably decreasing the flavor retention after spray-drying. Now, it turned out in the present case that, as shown in the examples below, the flavor retention of the product of the invention is not affected by the dilution rate, or solid content in the aqueous emulsion introduced into the spray-drier. In other words, high dilution rates may be employed in order to get a good monodispersity of the powder without provoking any drawback on the flavor retention, which is a totally unexpected result.

[0037] The spray-drying apparatus used in the process of the invention can be any of the various commercially available apparatus. Examples of spray-drying apparatuses are the Anhydro Dryers (origin : Anhydro Corp. of Attleboro Falls, Mass.), the Niro Dryer (manufactured by Niro Atomizer Ltd., Copenhagen, Denmark), or a Leaflash apparatus (origin : CCM Sulzer). Preferably a spray-drier with a pressure nozzle is used.

[0038] The process will be described in a more detailed manner in Example 1. However, the parameters characteristic of a spray-drying process are well known in the art and can be easily adjusted by a skilled person in the art.

[0039] The particulates of the invention have typically a size comprised between 50 and 70 μm and a bulk density comprised between 0.4 and 0.6 g/cm^3. However, a skilled person in the art knows well that the granulometry and the bulk density of the resulting dry powders can be adjusted by selecting the nozzle pressure until the powder having the desired flowability is obtained.

[0040] The spray-dried powders prepared according to a process of the invention can be utilized as such in applications, for instance for the perfuming or flavoring of compositions wherein a release is induced by shear or heat. However, they also can be advantageously used as starting materials to be subjected to further processing, before being used as delivery systems in a variety of applications.

[0041] In particular, in one embodiment of the invention, the spray-dried particles obtained by the method here-above described, are further encapsulated in an extruded glassy matrix which may be formed from one or more carbohydrate materials or which may just comprise a plasticizer and an emulsifying agent, in order to produce a glassy matrix with an improved thermal stability. US 5,087,461, the contents of which is hereby included by reference, describes and exemplifies

an encapsulation method of a spray-dried composition by way of extrusion. This process leads to narrow rods having a diameter in the range of 0.3 to 3 mm.

[0042] Apart from the extrusion, other kinds of encapsulation processing, following the spray-drying, are possible. The powder obtained can for instance be submitted to a second spray-drying, thus providing a two-stage spray-dried product. This technique in particular, as well as multi-stage spray-drying in general, are described by W.J. Coumans, P.J.A.M. Kerkhof and S. Bruin in Drying Technology, Vol. 12 (1 and 2), (1994), the teaching of which is hereby included by reference.

[0043] These examples are not restrictive of the encapsulation techniques which can be used for further processing of the spray-dried powder obtained according to the present invention, notably with the aim of increasing the size of the particles, or improving a particular characteristic of the powder, in order to rend it suitable for specific applications.

[0044] The products of the invention, namely the spray-dried powder as such, as well as the spray-dried compositions further subjected to a second kind of encapsulation can be advantageously used for instance for the perfuming or flavoring of food compositions in particular.

[0045] Therefore, the delivery systems of the invention can be used in applications such as chewing gums or chewing sweets, savoury food or baking in the field of flavours. Similarly the field of perfumery comprises many applications where this kind of encapsulation systems may be very useful. For instance all kinds of deodorants and antiperspirants constitute suitable applications for a perfuming delivery system with a controlled release of the perfuming ingredient and wherein the integrity of the latter is desirable until consumer use of for a certain period of time.

[0046] The powder of the invention may also be advantageously used for perfuming powder bases such as detergent bases. In fact, as shown in a comparative example below, the encapsulation system here-disclosed presents a very good stability towards moisture or relative humidity and these products can therefore be stored during a long period of time before being used, without being subjected to a degradation of the encapsulated perfume.

[0047] In those applications, the compositions of the invention provide a flavor or fragrance retention of up to 85% after the encapsulation process, at a fix level as high as 50%, and in an unexpected manner, the flavor retention being independent of the solid content of the aqueous emulsion introduced into the spray-drier. Moreover, the product hydrates very slowly in water and does not dissolve up to two weeks.

[0048] The invention will be now described in a more detailed manner in the examples below, wherein the temperatures are indicated in degrees Celsius and the abbreviations have the usual meaning in the art.

Modes of Carrying out the Invention

Example 1

Preparation of a spray-dried composition according to the invention

Formulation :

[0049]

Ingredients	Grams	% dry
Maltodextrin 16DE	1729	24.70
Sucrose	1729	24.70
Agar agar	700	10.00
Lemon oil [1)]	2800	40.00
Lecithin	42	0.60
Water	13600	
Total		100.00

1) origin : Firmenich Citrus Center, Florida, USA

Preparation :

[0050] A batch was prepared by hydrating agar agar in water (approximately 10% solids level) and subsequently mixing it with the rest of the ingredients in a stainless kettle equipped with pneumatic agitation. The batch temperature was maintained at 65-70°. When the contents of the kettle were uniform, it was homogenized at 7000 kPa.

[0051] The prepared feed was dried with a Leaflash apparatus characterized by the respective inlet/outlet temperatures

of 180/80°; a feed pressure of $17x10^3$ Pa ; and a nozzle 70/216 (spraying system) (diameter of spray orifice/spinner nozzle).

[0052] Samples were collected and analyzed for oil content by steam distillation. The flavor retention of the particulates after the process was of 85% (solid content of the aqueous emulsion introduced into the spray-drier of 33.98%).

[0053] Hydration characteristics and oil droplets release were investigated by microscopy. Thus, after 2 weeks in water, no oil coming out of the powder was observed. The particulates were intact.

Example 2

Preparation of a spray-dried composition according to the invention

Formulation :

[0054]

Ingredients	Grams	% dry
Maltodextrin 18DE	1379	19.70
Sucrose	1379	19.70
Agar agar	700	10.00
Lemon oil [1)]	3500	50.00
Lecithin	42	0.60
Water	15200	
Total		100.00
1) see Example 1		

Preparation : The spray-dried powder was prepared as described in Example 1.

[0055] The final product (after the process) had a flavor retention of 87.80% (solid content of the aqueous emulsion introduced into the spray-drier of 31.53%). No oil droplets diffused from the particles after 2 weeks in water.

Example 3

Preparation of a spray-dried composition according to the invention

Formulation:

[0056]

Ingredients	Grams	% dry
Maltodextrin 18DE	1554	22.20
Sucrose	1554	22.20
Agar agar	1050	15.00
Lemon oil [1)]	2800	40.00
Lecithin	42	0.60
Water	23200	
Total		100.00
1) see Example 1		

Preparation : The spray-dried powder was prepared as described in Example 1.

[0057] The final product (after the process) had a flavor retention of 85.30% (solid content of the emulsion introduced into the spray-drier of 23.18%).
No oil droplets diffused from the particles after 2 weeks in water.

Example 4

Preparation of a spray-dried composition according to the invention

Formulation :

[0058]

Ingredients	Grams	%dry
Maltodextrin 18DE	798	11.40
Sucrose	1554	22.20
Agar agar	1050	15.00
Gum Arabic	798	11.40
Lemon oil [1)]	2800	40.00
Water	18200	
Total		100.00
1) see Example 1		

Preparation : The spray-dried powder was prepared as described in Example 1.

[0059] The final product (after the process) had a flavor retention of 87.00% (solid content of the emulsion introduced into the spray-drier of 27.78%).
No oil droplets diffused from the particles after 2 weeks in water.

Example 5

Preparation of a spray-dried composition according to the invention

Formulation :

[0060]

Ingredients	Grams	% dry
Maltodextrin 18DE	2079	29.70
Sucrose	2079	29.70
Agar agar	700	10.00
Fragrance [1)]	2100	30.00
Lecithin	42	0.60
Water	13600	
Total		100.00
1) origin : Firmenich SA, Geneva, Switzerland		

Preparation : The spray-dried powder was prepared as described in Example 1.

[0061] The final product (after the process) had a flavor retention of 100% (solid content of the emulsion introduced into the spray-drier of 33.98%).
No oil droplets diffused from the particles after 2 weeks in water.

Example 6

Spray-dried composition of the invention, further extruded in a glassy matrix

[0062] A spray-dried composition was prepared as described in Example 1 from the following formulation :

Ingredients	% dry
Maltodextrin 18 DE	84
Agar agar	5
Orange oil	1
Citrem	5
Neobee	5
Total	100

[0063] The obtained powder was extruded under $2x10^5$ Pa pressure through a die plate with 0.8 mm diameter holes at a temperature of 95°.

Example 7

Comparative example on the stability of a spray-dried composition according to the invention, in a detergent base

[0064] Two spray-dried compositions having the following formulations were prepared according to the method described in Example 1 :

Formulation A :

[0065]

Ingredients	Grams	% dry
Maltodextrin 18DE	2865	38.20
Sucrose	2865	38.20
Perfume composition [1)]	1500	20.00
Agar agar	225	3.00
Lecithin	45	0.60
Water Total	9600	100.00

1) composition consisting of a mixture of benzyl acetate, phenylethyl acetate, cyclamen aldehyde, Lilial® (origin: Givaudan-Roure, Vernier, Switzerland) and hexyl salicylate ; each ingredient being present in the same weight percentage in the composition

Formulation B :

[0066]

Ingredients	Grams	% dry
Maltodextrin 18DE	2977.5	39.70
Sucrose	2977.5	39.70
Perfume composition [1)]	1500.0	20.00
Lecithin	45.0	0.60
Water	9600.0	

(continued)

Ingredients	Grams	% dry
Total		100.00
1) see *Formulation A*		

[0067] Each powder was independently admixed with a standard European detergent powder with percarbonate-TAED bleaching system. After a four weeks storage at 37° and 70% relative humidity, the two compositions were respectively separated from the detergent, dissolved in water, and diluted with acetonitrile and 2-heptanone. 1 G of the solution thus obtained was dried over 5 g of Na_2SO_4 and the residual liquid phase was analysed by a standard GC-MS analytical method to determine the residual quantity of the various perfuming ingredients. The results were compared with those obtained with a reference detergent, stored for four weeks at 3°, on which the perfume composition was directly sprayed-on. The results are summarised in Table 1.

Table 1 : Percentage of perfume ingredients recovered after storage for four weeks at 37° and 70% RH

Perfuming ingredient	Sprayed-on detergent powder	Formulation B (no agar agar)	Formulation A (3% of agar agar)
Benzyl acetate	3	6	6
Phenyl ethyl acetate	10	18	23
Cyclamen aldehyde	31	45	67
Lilial®	0.0	2	10
Hexyl salicylate	25	48	100

[0068] The results reported in Table 1 demonstrate the superiority of the spray-dried composition comprising agar agar which , after a month period of storage, contains the highest proportion of perfuming ingredients which have not been decomposed.

Claims

1. A spray-dried composition, comprising one or more active ingredients dispersed in a carrier, wherein said carrier comprises at least one wall-forming carbohydrate material and from 1 to 30% by weight of agar agar, relative to the dried weight of the composition.

2. A spray-dried composition according to claim 1, wherein the carrier comprises from 1 to 20% by weight of agar agar, relative to the dried weight of the composition.

3. A spray-dried composition according to claim 1, wherein the carrier comprises from 1 to 15% by weight of agar agar, relative to the dried weight of the composition.

4. A spray-dried composition according to claim 1, wherein the wall-forming carbohydrate material is selected from the group consisting of maltodextrin, corn syrup, chemically modified starch, hydrogenated starch hydrolysate, and succinylated or hydrolyzed starch.

5. A spray-dried composition according to claim 4, wherein the wall forming consists of maltodextrin.

6. A spray-dried composition according to claim 1, which comprises from 0.01 to 50% of a plasticiser selected from the group consisting of a mono- and a disaccharide.

7. A spray-dried composition according to claim 5, which comprises from 0.01 to 50% of a plasticiser selected from the group consisting of a mono- and a disaccharide.

8. A spray-dried composition according to claim 1, which comprises from 1 to 30% by weight of an emulsifier, relative to the dried weight of the composition.

9. A spray-dried composition according to claim 1, wherein the active ingredient is a perfuming ingredient.

10. A spray-dried composition according to claim 1, wherein the active ingredient is a flavoring ingredient.

11. A spray-dried composition according to claim 1, comprising from 1 to 60% of active ingredient relative to the dried weight of the composition.

12. A spray-dried composition according to claim 11, comprising from 20 to 50% of active ingredient relative to the dried weight of the composition.

13. A method for the preparation of a particulate product, comprising the steps of

a) forming an aqueous emulsion of an active ingredient dispersed in a carrier comprising at least one wall-forming carbohydrate material and from 1 to 30% of agar agar ;
b) homogenizing the emulsion ;
c) spray-drying the emulsion to form a particulate product.

14. A method according to claim 13, wherein step c) is carried out by using a spray-drying apparatus equipped with a pressure nozzle.

15. A method according to claim 13, wherein the particulate product formed in step c) is further encapsulated.

16. A method according to claim 15, wherein the encapsulation consists in extruding the particulate product in a glassy matrix to form a granular delivery system.

17. A granular delivery system obtainable by a method according to claim 16.

18. A method according to claim 15, wherein the encapsulation consists in spray-drying the particulate product in order to form a multi-stage spray-dried powder.

19. A multi-stage spray-dried powder obtainable by a method according to claim 18.

20. A method for flavoring a food or beverage product, which comprises adding a spray-dried composition according to claim 10, to said food or beverage product.

21. A method for flavoring or a food, or beverage product, which comprises adding a granular delivery system according to claim 17, to said food or beverage product.

22. A method for improving, enhancing or modifying the fragrance properties of a composition, wherein a spray-drying composition according to claim 9 is added to said composition.

23. A food or beverage product, **characterised in that** it comprises a composition according to claim 10.

24. A perfumed product or article, **characterised in that** it comprises a composition according to claim 9.

25. A perfumed article according to claim 24, in the form of a powdered detergent.

Patentansprüche

1. Sprühgetrocknete Zusammensetzung, aufweisend einen oder mehrere aktive Bestandteile, die in einem Träger dispergiert sind, wobei der Träger mindestens ein eine Hülle bildendes Kohlenhydratmaterial aufweist, sowie bezogen auf die Trockenmasse der Zusammensetzung 1% bis 30 Gew.% Agar-Agar.

2. Sprühgetrocknete Zusammensetzung nach Anspruch 1, wobei der Träger 1% bis 20 Gew.% Agar-Agar bezogen auf die Trockenmasse der Zusammensetzung aufweist.

3. Sprühgetrocknete Zusammensetzung nach Anspruch 1, wobei der Träger 1% bis 15 Gew.% Agar-Agar bezogen

auf die Trockenmasse der Zusammensetzung aufweist.

4. Sprühgetrocknete Zusammensetzung nach Anspruch 1, wobei das eine Hülle bildende Kohlenhydratmaterial ausgewählt ist aus der Gruppe, bestehend aus: Maltodextrin, Maisstärkesirup, chemisch modifizierte Stärke, hydriertes Stärkehydrolysat und succinylierte oder hydrolysierte Stärke.

5. Sprühgetrocknete Zusammensetzung nach Anspruch 4, wobei das eine Hülle bildende Kohlenhydratmaterial aus Maltodextrin besteht.

6. Sprühgetrocknete Zusammensetzung nach Anspruch 1, welche 0,01% bis 50% eines Weichmachers aufweist, der ausgewählt ist aus der Gruppe, bestehend aus einem Mono- und einem Disaccharid.

7. Sprühgetrocknete Zusammensetzung nach Anspruch 5, welche 0,01% bis 50% eines Weichmachers aufweist, der ausgewählt ist aus der Gruppe, bestehend aus einem Mono- und einem Disaccharid.

8. Sprühgetrocknete Zusammensetzung nach Anspruch 1, welche bezogen auf die Trockensubstanz der Zusammensetzung 1% bis 30 Gew.% Emulgiermittel aufweist.

9. Sprühgetrocknete Zusammensetzung nach Anspruch 1, wobei der aktive Bestandteil ein parfümierender Bestandteil ist.

10. Sprühgetrocknete Zusammensetzung nach Anspruch 1, wobei der aktive Bestandteil ein aromatisierender Bestandteil ist.

11. Sprühgetrocknete Zusammensetzung nach Anspruch 1, aufweisend bezogen auf die Trockenmasse der Zusammensetzung 1% bis 60% des aktiven Bestandteils.

12. Sprühgetrocknete Zusammensetzung nach Anspruch 11, aufweisend bezogen auf die Trockenmasse der Zusammensetzung 20% bis 50% des aktiven Bestandteils.

13. Verfahren zum Herstellen eines partikulären Produktes, umfassend die Schritte:

    a) Erzeugen einer wässrigen Emulsion eines aktiven Bestandteils, das in einem Träger dispergiert ist, aufweisend mindestens ein eine Hülle bildendes Kohlenhydratmaterial und 1% bis 30% Agar-Agar;
    b) Homogenisieren der Emulsion;
    c) Sprühtrocknen der Emulsion zur Erzeugung eines partikulären Produktes.

14. Verfahren nach Anspruch 13, wobei Schritt c) ausgeführt wird, indem ein Apparat zum Sprühtrocknen verwendet wird, der mit einer Druckdüse ausgestattet ist.

15. Verfahren nach Anspruch 13, wobei das in Schritt c) erzeugte partikuläre Produkt ferner verkapselt wird.

16. Verfahren nach Anspruch 15, wobei die Verkapselung in einem Extrudieren des partikulären Produkts zu einer glasartigen Matrix unter Erzeugung eines granulären Zuführsystems besteht.

17. Granuläres Zuführsystem, das mit Hilfe des Verfahrens nach Anspruch 16 erhalten werden kann.

18. Verfahren nach Anspruch 15, wobei die Verkapselung im Sprühtrocknen des partikulären Produktes besteht, um ein mehrstufig sprühgetrocknetes Pulver zu erzeugen.

19. Mehrstufig sprühgetrocknetes Pulver, das mit Hilfe eines Verfahrens nach Anspruch 18 erhalten werden kann.

20. Verfahren zum Aromatisieren eines Lebensmittel- oder Getränkeproduktes, welches Verfahren das Zusetzen einer sprühgetrockneten Zusammensetzung nach Anspruch 10 zu dem Lebensmittel- oder Getränkeprodukt umfasst.

21. Verfahren zum Aromatisieren eines Lebensmittel- oder Getränkeprodukts, welches Verfahren das Zusetzen eines granulären Zuführsystems nach Anspruch 17 zu dem Lebensmittel- oder Getränkeprodukt umfasst.

22. Verfahren zum Verbessern, Verstärken oder Modifizieren der Dufteigenschaften einer Zusammensetzung, bei welchem Verfahren eine sprühtrocknende Zusammensetzung nach Anspruch 9 der Zusammensetzung zugegeben wird.

23. Lebensmittel- oder Getränkeprodukt, **dadurch gekennzeichnet, dass** es eine Zusammensetzung nach Anspruch 10 aufweist.

24. Parfümiertes Produkt oder parfümierter Artikel, **dadurch gekennzeichnet, dass** es/er eine Zusammensetzung nach Anspruch 9 aufweist.

25. Parfümierter Artikel nach Anspruch 24 in Form eines pulverförmigen Waschmittels.

Revendications

1. Composition séchée par pulvérisation, comprenant un ou plusieurs ingrédients actifs dispersés dans un support, dans laquelle ledit support comprend au moins une matière glucidique formant une paroi et de 1 à 30% en poids d'agar-agar, relativement au poids séché de la composition.

2. Composition séchée par pulvérisation suivant la revendication 1, dans laquelle le support comprend de 1 à 20% en poids d'agar-agar, relativement au poids séché de la composition.

3. Composition séchée par pulvérisation suivant la revendication 1, dans laquelle le support comprend de 1 à 15% en poids d'agar-agar, relativement au poids séché de la composition.

4. Composition séchée par pulvérisation suivant la revendication 1, dans laquelle la matière glucidique formant une paroi est choisie dans le groupe constitué de maltodextrine, de sirop de maïs, d'amidon chimiquement modifié, d'hydrolysat d'amidon hydrogéné et d'amidon succinylé ou hydrolysé.

5. Composition séchée par pulvérisation suivant la revendication 4, dans laquelle la matière glucidique formant une paroi est constituée de maltodextrine.

6. Composition séchée par pulvérisation suivant la revendication 1, qui comprend de 0,01 à 50% d'un plastifiant choisi dans le groupe constitué d'un mono- et d'un disaccharide.

7. Composition séchée par pulvérisation suivant la revendication 5, qui comprend de 0,01 à 50% d'un plastifiant choisi dans le groupe constitué d'un mono- et d'un disaccharide.

8. Composition séchée par pulvérisation suivant la revendication 1, qui comprend de 1 à 30% en poids d'un émulsifiant, relativement au poids séché de la composition.

9. Composition séchée par pulvérisation suivant la revendication 1, dans laquelle l'ingrédient actif est un ingrédient parfumant.

10. Composition séchée par pulvérisation suivant la revendication 1, dans laquelle l'ingrédient actif est un ingrédient aromatisant.

11. Composition séchée par pulvérisation suivant la revendication 1, comprenant de 1 à 60% d'ingrédient actif relativement au poids séché de la composition.

12. Composition séchée par pulvérisation suivant la revendication 11, comprenant de 20 à 50% d'ingrédient actif relativement au poids séché de la composition.

13. Procédé pour la préparation d'un produit particulaire, comprenant les étapes:

a) de formation d'une émulsion aqueuse d'un ingrédient actif dispersé dans un support comprenant au moins une matière glucidique formant une paroi et de 1 à 30% d'agar-agar;
b) d'homogénéisation de l'émulsion;

c) de séchage par pulvérisation de l'émulsion pour former un produit particulaire.

14. Procédé suivant la revendication 13, dans lequel l'étape c) est réalisée en employant un appareil de séchage par pulvérisation équipé avec une buse de pression.

15. Procédé suivant la revendication 13, dans lequel le produit particulaire formé dans l'étape c) est en outre encapsulé.

16. Procédé suivant la revendication 15, dans lequel l'encapsulation consiste à extruder le produit particulaire dans une matrice vitreuse pour former un système de relargage granulaire.

17. Système de relargage granulaire pouvant être obtenu par un procédé suivant la revendication 16.

18. Procédé suivant la revendication 15, dans lequel l'encapsulation consiste à sécher par pulvérisation le produit particulaire dans le but de former une poudre séchée par pulvérisation à étapes multiples.

19. Poudre séchée par pulvérisation à étapes multiples pouvant être obtenue par un procédé suivant la revendication 18.

20. Procédé pour l'aromatisation d'un produit alimentaire ou à boire, qui comprend l'ajout d'une composition séchée par pulvérisation suivant la revendication 10 audit produit alimentaire ou à boire.

21. Procédé pour l'aromatisation d'un produit alimentaire ou à boire, qui comprend l'ajout d'un système de relargage granulaire suivant la revendication 17 audit produit alimentaire ou à boire.

22. Procédé pour améliorer, accroître ou modifier les propriétés de fragrance d'une composition, dans lequel une composition de séchage par pulvérisation suivant la revendication 9 est ajoutée à ladite composition.

23. Produit alimentaire ou à boire, **caractérisé en ce qu'**il comprend une composition suivant la revendication 10.

24. Produit ou article parfumé, **caractérisé en ce qu'**il comprend une composition suivant la revendication 9.

25. Article parfumé suivant la revendication 24, sous la forme d'un détergent en poudre.

REFERENCES CITED IN THE DESCRIPTION

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(54) Method for the preparation of a spray dried fat powder

(57) The invention relates to:
- Method for the preparation of a spray dried fat powder from an oil in water emulsion (O/W emulsion) by using an emulsifier, whereby under circumstances, commonly used for spray drying, an emulsion of an acidified water phase and a fat phase are converted, in which gluten is being used as an emulsifier, from which at least at least 3% of the disulphide bridges are reversibly broken, and wherein the water phase contains at least 0.01 percent of weight of a reducing agent based on the amount of gluten..
- a spray dried fat powder, obtainable by the mentioned procedure.

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Description

Introduction:

[0001] The current invention relates to a method to prepare fat powder from an oil in water emulsion by spray drying. More specifically, it relates to a method wherein gluten is used as emulsifier. The gluten as used in this invention is known as native or vital gluten, which definition excludes enzymatically hydrolyzed or chemically deamidated gluten.

State of the art:

[0002] Casein is an animal protein, present in milk. Casein, or actually a caseinate compound of that, is amongst others used in the food industry to serve as an emulsifier (surface active substance) for the preparation of fat and oil products which are used in powder form.

[0003] Other applications of fat powder are for example as coffee creamer and as bakery raw material. Casein is, however, expensive. An idea from US5767107 is to replace casein by gluten. Gluten is an amorphous protein which, combined with starch, can be found in the endosperm of different grains (for example wheat, rye, barley) and the products made thereof. The disadvantage of gluten is that it does not dissolve well in water, which is necessary to use it as an emulsifier, and that it is highly viscous in the solution. This limits the possibilities for the application of gluten.

[0004] Instead of using (sodium)caseinate, enzymatically hydrolyzed or chemically deamidated gluten have been used. However, both of these products have the disadvantage that their commercial prices are significantly higher than those of native / vital gluten.

A significant difference between native gluten and these products is that both hydrolyzed and deamidated products are degraded in an irreversible and permanent manner. Furthermore, products based on hydrolyzed or chemically deamidated gluten, or even based on (sodium)caseinate, will not result in a powder that gives a stable dispersion after reconstitution in an acidic medium.

[0005] It is part of the current invention to find a good substitute for caseinate, i.e. to find a suitable emulsifier for the preparation of a fat powder by spray drying, whereby the functionality of the fat powder remains similar. Despite the disadvantages of gluten (low solubility, agglomeration in an aqueous environment) this goal has been accomplished, by on the one hand treating the gluten in such a way that they remain highly suitable for the encapsulation of oils or fats, whilst on the other hand , the gluten do not retain their original high viscosity anymore, which is detrimental for spray-drying. To achieve this the gluten does not have to be deamidated and/or be treated enzymatic. An additional advantage is that the new product may contain solely vegetable raw material. Indeed, consumers prefer more natural /less modified products.

The use of gluten is known.

[0006] US patent 5,767,107, mentioned before, describes compositions containing gluten and polysaccharides that contain uronic acid residues, which are useful for encapsulating fats, oils and solids. Claimed is the encapsulation of vitamins. Specific to this patent is the use of carbohydrates containing uronic acid, in order to influence the properties of the protein. In contrast to the composition described in the current patent, preparation is done at a neutral pH.

[0007] WO0011973 refers to the application of soluble wheat protein for the preparation of a spray dried emulsified topping base. Soluble wheat protein is a product obtained by deamidation or enzymatic degradation (hydrolysis). Deamidation is an irreversible chemical modification which takes place at high temperatures (appr. 100°C or above), under the influence of H^+ or OH^-. Through this reaction amide groups on the protein are converted to carboxylic acid groups, causing the glutamines (gluten) to permanently loose their ability to form hydrogen bridges. This increases the solubility of the gluten in water at neutral pH. After deamidation a product is formed with properties very different from those of native gluten.

[0008] EP0301278 describes a method for making a "particle dispersing agent" which comprises a protein partial degradation product, useful for reducing viscosity of an aqueous dispersion wherein various water insoluble or sparingly soluble inorganic and/or organic particles are suspended. The treatment with sodium sulphite at temperatures up to 120°C causes severe hydrolysis and deamidation of the proteins,. This patent hence does not relate to processes using native gluten.

[0009] EP1602282 relates to "a foamable water in oil type emulsion composition for use in buttercreams or like products and to a method of producing the same". This comprises of a product which, in contrast to the objective of the current patent, is not (spray)dried.

[0010] EP0372669 relates to "A stabilized oil and fat powder comprises one or both of gliadin and glutenin and an oil and/or fat. The oil and fat may be partially or entirely clathrated and/or coated with gliadin and/or glutenin". In this patent alcohol is being used as a solvent, whereas in the current patent merely aqueous solvents are used.

[0011] A common problem to these prior art processes concerns the high viscosity of the gluten, which problem has been solved by the present inventors.

Short definition of the invention:

[0012] Method for the preparation of spray dried fat powder from an oil in water emulsion (O/W emulsion) by using an emulsifier, whereby under circumstances, common for spray drying, an emulsion of an acidified water phase and a fat phase are converted, whereby gluten is being used as an emulsifier, from which at least 3% of the disulphide bridges are reversibly broken, and wherein the water phase contains at least 0.01 percent of weight of a reducing agent.

Modes for carrying out the invention:

[0013] The current invention relates to a method to prepare fat powder from an O/W emulsion by spray drying. This fat powder is made from edible oils and/or fats, for example from palm oil. The expert, however, knows about various oils and fats that may be applied.

[0014] The method includes the preparation of an oil in water emulsion from an oil or fat on the one hand, and an aqueous phase, in general a glucose syrup (for example from Syral), on the other hand, in the presence of an adequate emulsifier. Next, this emulsion is spray dried to prepare dry powder using commonly applied conditions and equipment. Due to the presence of an emulsifier a (stable) emulsion can emerge, whereby the emulsifier can arrange itself around the fat droplets in the aqueous environment. During spray drying the emulsifier also forms a small film around the fat droplets. The protecting film makes sure that the powder can be used without fouling ("good free-flowing") and that the fat and/or oil, of which the fatty acids typically are partly unsaturated, is protected against oxidation and other influences.

[0015] Spray drying equipment is supplied by for example Niro, and/or BMA. The O/W-emulsion is spray dried under similar circumstances as the fat powders made with (enzymatically) hydrolysed or deamidated gluten, or casein as emulsifier. Generally an air inlet temperature in the spray dryer between 150°C and 200°C, preferably about 180°C, and a spray pressure between 100 and 150 bar, preferably about 130 bar, are used. The preferred dry matter content is as high as possible and is, for economical reasons, preferably above 50%-60%.

[0016] Primary dispersion of the oil in water phase is preferably done by dispersing very intensively, for example under the influence of high pressure. The best results are achieved with a high shear mixer. There are mixers of various forms. Silverson mixers are frequently used mixers and very suitable for the method of the current invention. In this way a relatively stable (pre-)emulsion is made.

[0017] It is presumed that the shear forces and turbulent forces make sure that the fat droplets in the pre-emulsion are reduced in size and dispersed in the water phase. Furthermore the dispersing forces allow the gluten to find a place on the fat surface thus stabilizing the emulsion against immediate coalescence. It is not strictly necessary to intensively disperse the oil prior to the actual homogenisation step, but it significantly reduces the risk of phase separation before the high pressure homogenisation step that normally follows after making the pre-emulsion.

[0018] By preference the pre-emulsion is therefore subsequently homogenised. During homogenisation, for example by using a high pressure homogeniser, the fat droplets are further reduced in size. The problem of gluten dispersions normally produced is that the viscosity is too high to pump and/or spray the emulsion during the production process. This problem is solved by reducing the disulfide bridges in the gluten by adding a reductor,for example cysteine.

[0019] As is commonly applied, the aqueous phase preferably exists of an aqueous solution of one or more mono-, oligo- and/or polysaccharides (separately or jointly referred to as sugar), preferentially an aqueous solution which contains 50-80 weight percentage of sugar. Various sugars are suitable. Common is the application of maltodextrin, lactose, glucose syrup, dextrose, fructose and/or saccharose.

[0020] According to the invention, the water phase contains an acid in such an amount that the pH of the water phase is smaller than 6, preferably between 1,5 and 4. The acid may be an organic or inorganic acid or a combination of organic and/or anorganic acids, preferably an acid or combination of acids which are approved for applications in the food industry. Examples of convenient organic acids are acetic acid, formic acid, lactic acid, sorbic acid, benzoic acid, tartaric acid, succinic acid, malic acid, adipic acid, fumaric acid, citric acid, ascorbic acid. Examples of convenient inorganic acids are silicic acid, phosphoric acid, sulphuric acid and hydrochloric acid. This acidification has an important positive effect on the solubility of the gluten.

[0021] Gluten is a commercial product, manufactured from various vegetable sources and which can be used in each desirable form, as long as it is unmodified. Gluten originates preferably from wheat starch, maize starch or soya starch. Especially gluten from wheat is very suitable.

[0022] The use of an acidified water phase provides that the viscosity of the gluten is manageable. For this the gluten has to be brought in contact with the acidified water phase long enough. Acceptable conditions are contact during 1 to 240 minutes at a temperature between 5°C and 80°C, preferably between 50°C and 70°C and at a pH lower than 6, preferably between 1 and 4 (measured at room temperature).

[0023] The temperature during the process is preferably 60°-70°C. If so desired, this could be lower, for example if an oil is used which does not crystallise at room temperature, such as for example soybean or olive oil. However, at lower temperatures, the viscosity will increase.

[0024] The pH is important to get the wheat proteins to dissolve in the water phase. Currently a maximum value of 4 is preferred. However, this does not exclude the possibility to use a higher pH value, e.g. 5, in the end product.

[0025] According to the method of the current invention at least a part of the disulphide bridges of the gluten is broken in a reversible manner. This is possible by adding for example at least 0,01 weight percent (as a proportion of the amount of gluten) of a reducing agent. Adding the gluten to the aqueous phase, leads to the in-situ reversible reduction of these gluten. Next, the gluten can be dispersed, so that a homogenous dispersion or a solution is attained. Breaking the disulphide bridges leads to a decrease in the viscosity of the aqueous phase, and through that also of the emulsion obtained. This has a positive effect on the spray drying process. Also, this allows the use of a high dry matter content in the emulsion, that would otherwise lead to a too high viscosity and as a result thereof would be unsuitable for spray drying.

[0026] The number of free thiol groups in both untreated and cysteine treated gluten may be determined photometrically with DTNB (5-5"-dithio(2-nitrobenzoate) at 410 nm according to the Method of Ellman (1959). Ellman, G. L. (1959) Arch. Biochem. Biophys. 82, 70-77. The total number of cysteine residues in gluten may be determined using amino acid hydrolysis after performic acid oxidation by an automated two-step pre-column derivatization with two different reagents, OPA (o-phthalaldehyde) for primary and FMOC (9-fluorenylmethylchloroformate) for secondary amino acids according to Schuster(1988). Schuster, R. (1988) J. Chromatog. 431, 271-284

[0027] Adding cysteine or other reducing agents causes the viscosity of the emulsion to decrease.

[0028] The reducing agent is preferably, but not restricted to an organic or inorganic peroxide, and/or an alkaline (earth) metal bromide, iodide, oxide or sulphide, and/or an organic sulphide, glutathione, preferably cysteine. An at first glance unexpected but very positive effect of cysteine is, that the reversibly broken disulphide bridges will reform during spray drying (through the oxidising effect of oxygen in the air). This will improve the protective coating of the fat powder.

[0029] The oil in water emulsion is a common emulsion. Preferably this emulsion, consists per 100 parts by weight emulsion of:

- 10 to 80, preferably 15 to 40 parts by weight water phase,
- 90 to 20 preferably 85 to 60 parts by weight fat phase;
- 0,2 to 20 preferably 1 to 5 parts by weight gluten
- 1 to 10, preferably 2 to 5 weight percent of acid calculated on the quantity of gluten.

[0030] Because the viscosity of the emulsion according to the current invention, by application of dissolved reduced gluten as emulsifier, can be kept low, the emulsion may contain considerably more dry matter than if the gluten was applied in its non-reduced form; i.e. a form in which the disulphide bridges remain virtually intact. Because of this the dry matter content can be raised for example from 65% to 67-68% or more.

[0031] Spray drying preferably takes place under oxidative conditions, preferably in the presence of air, as a result of what at least a part of the broken disulphide bridges will be converted again to disulphides. This may be achieved, for example, by adding ascorbic acid to the emulsion as acidifier. Ascorbic acid will be converted to dehydroascorbic acid during the spray drying. The dehydroascorbic acid may cause the disulfde bridges at least partially to be repaired. This results in a strengthened emulsifying coating around the spray dried fat droplets. The expert will know how to apply oxidative conditions.

[0032] The invention also concerns the spray dried fat powder prepared according to the current invention. This fat powder distinguishes itself by the presence of gluten in the powder parts and the residue of a reductor.

[0033] As mentioned before, the advantage of producing a fat powder according to the method of this invention over the products based on prior art alternatives, is that the powder is soluble (dispersible) in an acidic medium at pH 4. This is shown in the next experiments

Examples

[0034] Spray drying took place under the following circumstances, in the course of which the fat powder according to method of preparation 1 or 2 was obtained.

Table 1: circumstances of spray drying

.t [min]	Tin [C]	T off [C]	Asp [%]	Pump [%]	Vac [mbar]
0	170	86	90	23	-50
3	170	102	100	23	-50
5	170	100	100	30	-50

(continued)

.t [min]	Tin [C]	T off [C]	Asp [%]	Pump [%]	Vac [mbar]
18	150	95	100	30	-50
35	150	95	100	40	-50
50	150	95	100	40	-50

Method of preparation 1

Percentages in weight%	
Dry matter in % in the emulsion	60-80
Maltodestrine/glucose syrup DE10-40	10-29,5
Citric acid (based on gluten)	2-5
Cysteine (based on gluten)	0,2-0,5
Gluten	0,5-5
fat	60-85

Method of preparation 2

Percentages in weight%	
Dry matter in % in the emulsion	60-80
Maltodestrine/glucose syrup DE10-40	35-79,5
Citric acid (based on gluten)	2-5
Cysteine (based on gluten)	0,2-0,5
Gluten	0,5-5
Fat	20-60

[0035] The glucose syrup was brought into the water at a pH of 6-8 and a temperature of 60-70°C, after which citric acid and cysteine was added. The pH decreased to pH 1-3,5. Next, the gluten and the palm oil were added, in the course of which the pH increased a little to pH 2-4.

[0036] The viscosity of the mixture was determined using a Brookfield Digital Viscometer model LVDVE230 equipped with a "Spindle 61" and a "guard leg" at an emulsion temperature of 50-60°C. The viscosity was as follows:

90 cps by 2,5 rpm
300 cps by 4,0 rpm
330 cps by 6,0 rpm
200 cps by 20,0 rpm

[0037] Subsequently, a emulsion was made using homogenization, after which the viscosity of the emulsion obtained was as follows:

1200 cps by 2,5 rpm
1300 cps by 3,0 rpm
1000 cps by 4,0 rpm
940 cps by 5,0 rpm

[0038] When cysteine was left out, the viscosity became appr.5000 cps at 2,5 rpm which is so high, that the emulsion could not be properly pumped anymore, making spray drying impossible.

Experiment:

[0039] A composition of spray dried powdered products based on prior art methods is as follows (% are percentages by weight): 80% fat/oil, 16-18% maltodextrin, 2% other components, 2% emulsifier / emulsion stabilizer. The emulsifier/ emulsion stabilizer may e.g. be one of the following products: sodium caseinate, or chemically deamidated gluten. These products are known and/or commercially available.

[0040] The above mentioned spray dried powders containing approx 80% fat, have been compared with the product obtained by the method of the current invention. For this comparison 5-30% dispersions /solutions are made in water with a temperature of 20-40 C. The properties of these dispersions are summarized in the Table below.

Spray dried powders containing approx 80% fat with emulsifier /stabilizer mentioned below:	**Stability of the solution / dispersion**
	pH 4
Sodium caseinate	--
Deamidated gluten	--
Product obtained by the method of this invention	+
"+"Is given when the dispersion /solution does remains stable; i.e. it does not separate. "-" Is given when separation is observed.	

Claims

1. Method for the preparation of a spray dried fat powder from an oil in water emulsion (O/W emulsion) by using an emulsifier, whereby under circumstances, commonly used for spray drying, an emulsion of an acidified water phase and a fat phase are converted, in which gluten is being used as an emulsifier, from which at least at least 3% of the disulphide bridges are reversibly broken, and wherein the water phase contains at least 0.01 percent of weight of a reducing agent based on the amount of gluten.

2. Method according to claim 1, comprising several steps, in which in step 1 a dispersion of the water phase and the gluten is made, preferably a finely homogenised dispersion or a solution; in which in step 2 an O/W emulsion of the product from step 1 and the fat phase is made, preferably a homogenised emulsion; and in which in step 3 the emulsion is spray dried until a water content is obtained of less then 15 weight percent, preferably less then 10 weight percent, calculated on the spray dried product.

3. Method according to claim 2, in which the water phase contains an acid in such an amount that the pH of the water phase is smaller than 6, preferably between 2 and 4.

4. Method according to one of the claims 1-3, in which the water phase contains at least 0,01 percent of weight of cysteine, based on the amount of gluten, wherein the gluten is added to the water phase and the gluten is reduced in-situ, followed up by a mixing step
in which the gluten is mixed until a homogenised dispersion or a solution is reached.

5. Method according to one of the claims 1-4, in which wheat starch, maize starch or soya starch is used as an emulsifier.

6. Method according to one of the claims 1-5, in which the gluten is brought into contact with the acidified water phase during 1 to 240 minutes, preferably during 10 to 60 minutes, at a temperature between 5 and 80°C, preferably between 50 and 70°C, at a pH smaller than 6, preferably between 2 and 4 (measured at room temperature).

7. Method according tot claims 6, in which the acid is an organic or an inorganic acid or a combination of organic and/or inorganic acids, preferably an acid or combination of acids which is allowed for application in the food industry.

8. Method according to claims 7, in which the acid is organic, selected from one or more of acetic acid, formic acid, lactic acid, sorbic acid, benzoic acid, tartaric acid, succinic acid, malic acid or citric acid, adipic acid, fumaric acid, ascorbic acid, preferably citric acid and/or ascorbic acid.

9. Method according to claims 8, in which the acid is inorganic, selected from one of more of silicic acid, phosphoric acid, sulphuric acid and hydrochloric acid.

10. Method according tot one of the claims 1-9, in which the gluten is treated with a reducing agent, selected from one or more of an organic or anorganic peroxide, and/or alkaline (earth) metal bromide, iodide, oxide or sulphide, and/or an organic sulphide, glutathione, preferably cysteine.

11. Method according to one of the claims 1-10, in which 100 parts by weight emulsion, , consist of: 10 to 80, preferably 15 to 40 parts by weight water phase, 90 to 20 preferably 85 to 60 parts by weight fat phase; 0,2 to 20 preferably 1 to 5 parts by weight gluten 1 to 10, preferably 2 to 5 weight percent of acid calculated on the quantity of gluten.

12. Method according to one of the claims 1-11, in which as water phase a aqueous solution of one or more mono-, oligo- and/or polysaccharides will be applied.

13. Method according to claims 11, in which a aqueous solution of maltodextrine, lactose, glucose syrup, dextrose, fructose, and/or saccharose or a combination of two or more of these, will be used.

14. Method according tot one of the claims 1-13, in which the spray drying will take place under oxidative conditions, preferably in the presence of air, as a result of which at least a part of the broken disulphide bridges will be converted again to disulphides.

15. Spray dried fat powder obtained according to the method of claim 1-14, consisting of an emulsifier encapsulated oil, in which the emulsifier is gluten, which has not been irreversibly modified, neither chemically nor enzymatically, and of which at least 3% and preferably at least 10% of the disulphide bridges originally are being broken in a nonpermanent /reversible manner.

16. Spray dried fat powder as claimed in anyone of claims 1-14, containing a residue of a redactor, preferably of cysteine

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EUROPEAN SEARCH REPORT

Application Number
EP 08 16 7481

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	29 January 2009	De Jong, Ellen

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EPO FORM 1503 03.82 (P04C01)

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EUROPEAN SEARCH REPORT

Application Number
EP 08 16 7481

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 16 7481

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(54) Spray-drying process

(57) The present invention relates to a process for preparing a spray-dried powder comprising:
(i) anionic detersive surfactant; (ii) from 0wt% to 10wt% zeolite builder; (iii) from 0wt% to 10wt% phosphate builder; and (iv) from 3wt% to 15wt% silicate salt;
the process comprising the steps of: (a) heating an aqueous slurry to a temperature above 100°C to form a heated slurry; and (b) spraying the heated slurry at temperature above 100°C into a spray-drying tower; (c) spray-drying the slurry to form a spray-dried powder.

EP 2 138 567 A1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a spray-drying process.

BACKGROUND OF THE INVENTION

[0002] There is a recent trend in the laundry detergent industry to produce low-built laundry powders. These are typically produced by a spray-drying process. However, the low-built spray-dried powder produced by these spray-drying processes has a poor stability profile. This is exacerbated when a significant amount of silicate salt is present in the spray-dried powder. The Inventors have overcome this problem by heating the aqueous slurry above the boiling point of water, and spraying it at this elevated temperature into a spray-drying tower. The Inventors have found that the low built spray-dried powders produced by the process of the present invention exhibit an improved stability profile.

SUMMARY OF THE INVENTION

[0003] The present invention relates to a process as defined in claim 1.

DETAILED DESCRIPTION OF THE INVENTION

Process for preparing a spray-dried powder

[0004] The process comprises the steps of: (a) heating an aqueous slurry to a temperature above 100°C to form a heated slurry; and (b) spraying the heated slurry at temperature above 100°C into a spray-drying tower; (c) spray-drying the slurry to form a spray-dried powder.

[0005] Preferably, in step (a), the aqueous slurry is heated to a temperature above 105°C, or above 110°C, or above 115°C, or above 120°C, or even at least 123°C, or even above 125°C.

[0006] Preferably, the heated slurry is sprayed at a temperature above 105°C, or above 110°C, or above 115°C, or above 120°C, or even above 125°C into the spray-drying tower.

[0007] Preferably, the heated slurry is sprayed at a pressure of at least $4x10^6$ Pa, or at least $5x10^6$ Pa, or at least $6x10^6$ Pa, or at least $7x10^6$ Pa, or even at least $8x10^6$ Pa into the spray-drying tower.

[0008] Preferably, the slurry heated by the addition of saturated steam, typically at elevated pressure.

[0009] The slurry can be heated by a chemical or nuclear exothermic reaction. The slurry may be heated by solar energy.

[0010] Preferably, the slurry is heated by a chemical exothermic reaction, preferably an in-situ exothermic reaction, most preferably an in-situ exothermic neutralization reaction, such as the neutralization of an acid anionic surfactant precursor. The use of an in-situ exothermic reaction as a heat source avoids the problems of fouling the internal pipe surfaces that may occur when external direct heat is applied.

[0011] Preferably, the spray-dried powder is contacted with non-ionic detersive surfactant.

Spray-dried powder

[0012] The spray-dried powder comprises: (i) anionic detersive surfactant; (ii) from 0wt% to 10wt% zeolite builder; (iii) from 0wt% to 10wt% phosphate builder; and (iv) from 3wt% to 15wt% silicate salt. The spray-dried powder may also comprise carbonate salt.

[0013] The spray-dried powder typically comprises adjunct detergent ingredients.

Anionic detersive surfactant

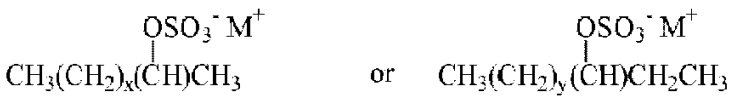
[0014] The anionic detersive surfactant preferably comprises alkyl benzene sulphonate. Preferably the anionic detersive surfactant comprises at least 50%, preferably at least 55%, or at least 60%, or at least 65%, or at least 70%, or even at least 75%, by weight of the anionic detersive surfactant, of alkyl benzene sulphonate. Preferably the alkyl benzene sulphonate is a linear or branched, substituted or unsubstituted, C_{8-18} alkyl benzene sulphonate. This is the optimal level of the C_{8-18} alkyl benzene sulphonate to provide a good cleaning performance. The C_{8-18} alkyl benzene sulphonate can be a modified alkylbenzene sulphonate (MLAS) as described in more detail in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548. Highly preferred C_{8-18} alkyl benzene sulphonates are linear C_{10-13} alkylbenzene sulphonates. Especially preferred are linear C_{10-13} alkylbenzene sulphonates that are obtainable, preferably obtained, by sulphonating commercially available linear alkyl

benzenes (LAB); suitable LAB include low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®.

[0015] The anionic detersive surfactant may preferably comprise other anionic detersive surfactants. A preferred adjunct anionic detersive surfactant is a non-alkoxylated anionic detersive surfactant. The non-alkoxylated anionic detersive surfactant can be an alkyl sulphate, an alkyl phosphate, an alkyl phosphonate, an alkyl carboxylate or any mixture thereof. The non-alkoxylated anionic surfactant can be selected from the group consisting of; C_{10}-C_{20} primary, branched-chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula:

$$CH_3(CH_2)_xCH_2\text{-}OSO_3^-M^+$$

wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations are sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9; C_{10}-C_{18} secondary (2,3) alkyl sulphates, typically having the following formulae:



wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations include sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9, y is an integer of at least 8, preferably at least 9; C_{10}-C_{18} alkyl carboxylates; mid-chain branched alkyl sulphates as described in more detail in US 6,020,303 and US 6,060,443; methyl ester sulphonate (MES); alpha-olefin sulphonate (AOS); and mixtures thereof.

[0016] Another preferred anionic detersive surfactant is an alkoxylated anionic detersive surfactant. The presence of an alkoxylated anionic detersive surfactant in the spray-dried powder provides good greasy soil cleaning performance, gives a good sudsing profile, and improves the hardness tolerance of the anionic detersive surfactant system. It may be preferred for the anionic detersive surfactant to comprise from 1% to 50%, or from 5%, or from 10%, or from 15%, or from 20%, and to 45%, or to 40%, or to 35%, or to 30%, by weight of the anionic detersive surfactant system, of an alkoxylated anionic detersive surfactant.

[0017] Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl alkoxylated sulphate having an average degree of alkoxylation of from 1 to 30, preferably from 1 to 10. Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 1 to 10. Most preferably, the alkoxylated anionic detersive surfactant is a linear unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 3 to 7.

[0018] The alkoxylated anionic detersive surfactant, when present with an alkyl benzene sulphonate may also increase the activity of the alkyl benzene sulphonate by making the alkyl benzene sulphonate less likely to precipitate out of solution in the presence of free calcium cations. Preferably, the weight ratio of the alkyl benzene sulphonate to the alkoxylated anionic detersive surfactant is in the range of from 1:1 to less than 5:1, or to less than 3:1, or to less than 1.7:1, or even less than 1.5:1. This ratio gives optimal whiteness maintenance performance combined with a good hardness tolerance profile and a good sudsing profile. However, it may be preferred that the weight ratio of the alkyl benzene sulphonate to the alkoxylated anionic detersive surfactant is greater than 5: 1, or greater than 6:1, or greater than 7:1, or even greater than 10:1. This ratio gives optimal greasy soil cleaning performance combined with a good hardness tolerance profile, and a good sudsing profile.

[0019] Suitable alkoxylated anionic detersive surfactants are: Texapan LEST™ by Cognis; Cosmacol AES™ by Sasol; BES151™ by Stephan; Empicol ESC70/U™; and mixtures thereof.

[0020] Preferably, the anionic detersive surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of the anionic detersive surfactant, of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate. Preferably the anionic detersive surfactant is essentially free of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate. By "essentially free of" it is typically meant "comprises no deliberately added". Without wishing to be bound by theory, it is believed that these levels of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate ensure that the anionic detersive surfactant is bleach compatible.

[0021] Preferably, the anionic detersive surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of alkyl sulphate. Preferably the anionic detersive surfactant is essentially free of alkyl sulphate. Without wishing to be bound by theory, it is believed that these levels of alkyl sulphate ensure that the anionic detersive surfactant is hardness tolerant.

Zeolite builder

[0022] The spray-dried powder typically comprises from 0% to 10wt% zeolite builder, preferably to 9wt%, or to 8wt%, or to 7wt%,or to 6wt%, or to 5wt%, or to 4wt%, or to 3wt%, or to 2wt%, or to 1wt%, or to less than 1% by weight of the spray-dried powder, of zeolite builder. It may even be preferred for the spray-dried powder to be essentially free from zeolite builder. By essentially free from zeolite builder it is typically meant that the spray-dried powder comprises no deliberately added zeolite builder. This is especially preferred if it is desirable for the spray-dried powder to be very highly soluble, to minimise the amount of water-insoluble residues (for example, which may deposit on fabric surfaces), and also when it is highly desirable to have transparent wash liquor. Zeolite builders include zeolite A, zeolite X, zeolite P and zeolite MAP.

Phosphate builder

[0023] The spray-dried powder typically comprises from 0% to 10wt% phosphate builder, preferably to 9wt%, or to 8wt%, or to 7wt%,or to 6wt%, or to 5wt%, or to 4wt%, or to 3wt%, or to 2wt%, or to 1wt%, or to less than 1% by weight of the spray-dried powder, of phosphate builder. It may even be preferred for the spray-dried powder to be essentially free from phosphate builder. By essentially free from phosphate builder it is typically meant that the spray-dried powder comprises no deliberately added phosphate builder. This is especially preferred if it is desirable for the composition to have a very good environmental profile. Phosphate builders include sodium tripolyphosphate.

Silicate salt

[0024] The spray-dried powder optionally comprises from 0% to 20wt% silicate salt, preferably from 1wt%, or from 2wt%, or from 3wt%, and preferably to 15wt%, or to 10wt%, or even to 5% silicate salt. Silicate salts include amorphous silicates and crystalline layered silicates (e.g. SKS-6). A preferred silicate salt is sodium silicate.

Carbonate salt

[0025] The spray-dried powder typically comprises carbonate salt, typically from 1% to 50%, or from 5% to 25% or from 10% to 20%, by weight of the spray-dried powder, of carbonate salt. A preferred carbonate salt is sodium carbonate and/or sodium bicarbonate. A highly preferred carbonate salt is sodium carbonate. Preferably, the spray-dried powder may comprise from 10% to 40%, by weight of the spray-dried powder, of sodium carbonate. However, it may also be preferred for the spray-dried powder to comprise from 2% to 8%, by weight of the spray-dried powder, of sodium bicarbonate. Sodium bicarbonate at these levels provides good alkalinity whilst minimizing the risk of surfactant gelling which may occur in surfactant-carbonate systems. If the spray-dried powder comprises sodium carbonate and zeolite, then preferably the weight ratio of sodium carbonate to zeolite is at least 15:1.

[0026] High levels of carbonate improve the cleaning performance of the composition by increasing the pH of the wash liquor. This increased alkalinity: improves the performance of the bleach, if present; increases the tendency of soils to hydrolyse, which facilitates their removal from the fabric; and also increases the rate, and degree, of ionization of the soils to be cleaned (n.b. ionized soils are more soluble and easier to remove from the fabrics during the washing stage of the laundering process). In addition, high carbonate levels improve the flowability of the spray-dried powder.

Adjunct detergent ingredients

[0027] Suitable adjunct ingredients include: detersive surfactants such as anionic detersive surfactants, nonionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants; preferred nonionic detersive surfactants are C_{8-18} alkyl alkoxylated alcohols having an average degree of alkoxylation of from 1 to 20, preferably from 3 to 10, most preferred are C_{12-18} alkyl ethoxylated alcohols having an average degree of alkoxylation of from 3 to 10; preferred cationic detersive surfactants are mono-C_{8-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides, more preferred are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C_{10-12} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride; source of peroxygen such as percarbonate salts and/or perborate salts, preferred is sodium percarbonate, the source of peroxygen is preferably at least partially coated, preferably completely coated, by a coating ingredient such as a carbonate salt, a sulphate salt, a silicate salt, borosilicate, or mixtures, including mixed salts, thereof; bleach activator such as tetraacetyl ethylene diamine, oxybenzene sulphonate bleach activators such as nonanoyl oxybenzene sulphonate, caprolactam bleach activators, imide bleach activators such as N-nonanoyl-N-methyl acetamide, preformed peracids such as N,N-pthaloylamino peroxycaproic acid, nonylamido peroxyadipic acid or dibenzoyl peroxide; enzymes such as amylases, carbohydrases, cellulases, laccases, lipases, oxidases,

peroxidases, proteases, pectate lyases and mannanases; suds suppressing systems such as silicone based suds suppressors; fluorescent whitening agents; photobleach; filler salts such as sulphate salts, preferably sodium sulphate; fabric-softening agents such as clay, silicone and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4-vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as hydrophobically modified cellulose and oligomers produced by the condensation of imidazole and epichlorhydrin; soil dispersants and soil anti-redeposition aids such as alkoxylated polyamines and ethoxylated ethyleneimine polymers; anti-redeposition components such as carboxymethyl cellulose and polyesters; perfumes; sulphamic acid or salts thereof; citric acid or salts thereof; and dyes such as orange dye, blue dye, green dye, purple dye, pink dye, or any mixture thereof.

EXAMPLES

[0028] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

Example 1. A spray-dried laundry detergent powder and process of making it.

Aqueous alkaline slurry composition.

[0029]

Component	Aqueous slurry (parts)
Sodium Silicate	8.5
Acrylate/maleate copolymer	3.2
Hydroxyethane di(methylene phosphonic acid)	0.6
Sodium carbonate	8.8
Sodium sulphate	42.9
Water	19.7
Miscellaneous, such as magnesium sulphate, and one or more stabilizers	1.7
Aqueous alkaline slurry parts	**85.4**

Preparation of a spray-dried laundry detergent powder.

[0030] An alkaline aqueous slurry having the composition as described above is prepared in a slurry making vessel (crutcher). The moisture content of the above slurry is 23.1 %. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. Saturated steam at a pressure of $6.0x10^5$ Pa is injected into the crutcher to raise the temperature to 90°C. The slurry is then transferred into a low pressure line (having a pressure of $5.0x10^5$ Pa).

[0031] Separately, 11.4 parts of linear alkylbenzene sulphonic acid (HLAS), and 3.2 parts of a 50w/w% aqueous sodium hydroxide solution are pumped into the low pressure line. In addition, saturated steam at a pressure of $6.0x10^5$ Pa is injected into the low pressure line*. The mixture is then pumped by a high pressure pump into a high pressure line (having an exit pressure of $8.0x10^6$ Pa). The mixture is then sprayed at a rate of 1,640kg/hour at a pressure of $8.0x10^6$ Pa and at a temperature of 125°C +/-2°C into a counter current spray-drying tower with an air inlet temperature of 275°C. The mixture is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.15mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 2.5wt%, a bulk density of 510 g/l and a particle size distribution such that greater than 80wt% of the spray-dried powder has a particle size of from 150 to 710 micrometers. The composition of the spray-dried powder is given below.

[0032] *The mass flow rate of saturated steam into the low pressure line is controlled by a temperature feedback controller that controls the temperature of the slurry entering the high pressure pump. The slurry temperature entering

the high pressure pump is maintained at 125°C +/- 2°C.

Spray-dried laundry detergent powder composition

[0033]

Component	%w/w Spray Dried Powder
Sodium silicate salt	10.0
Linear alkyl benzene sulphonate	15.1
Acrylate/maleate copolymer	4.0
Hydroxyethane di(methylene phosphonic acid)	0.7
Sodium carbonate	11.9
Sodium sulphate	53.7
Water	2.5
Miscellaneous, such as magnesium sulphate, and one or more stabilizers	2.1
Total Parts	**100.00**

[0034] A granular laundry detergent composition.

Component	%w/w granular laundry detergent composition
Spray-dried powder of example **1** (described above)	59.38
91.6wt% active linear alkyl benzene sulphonate flake supplied by Stepan under the tradename Nacconol 90G®	0.22
Citric acid	5.00
Sodium percarbonate (having from 12% to 15% active AvOx)	14.70
Photobleach particle	0.01
Lipase (11.00mg active/g)	0.70
Amylase (21.55mg active/g)	0.33
Protease (56.00mg active/g)	0.43
Tetraacetyl ethylene diamine agglomerate (92wt% active)	4.35
Suds suppressor agglomerate (11.5wt% active)	0.87
Acrylate/maleate copolymer particle (95.7wt% active)	0.29
Green/Blue carbonate speckle	0.50
Sodium Sulphate	9.59
Solid perfume particle	0.63
Ethoxylated C_{12}-C_{18} alcohol having an average degree of ethoxylation of 7 (AE7)	3.00
Total Parts	**100.00**

[0035] The above laundry detergent composition was prepared by dry-mixing all of the above particles (all except the AE7) in a standard batch mixer. The AE7 in liquid form is sprayed on the particles in the standard batch mixer. Alternatively, the AE7 in liquid form is sprayed onto the spray-dried powder of example 1. The resultant powder is then mixed with all of the other particles in a standard batch mixer.

[0036] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited

value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

Claims

1. A process for preparing a spray-dried powder comprising:

   (i) anionic detersive surfactant;
   (ii) from 0wt% to 10wt% zeolite builder;
   (iii) from 0wt% to 10wt% phosphate builder; and
   (iv) from 3wt% to 15wt% silicate salt;

   the process comprising the steps of:

   (a) heating an aqueous slurry to a temperature above 100°C to form a heated slurry; and
   (b) spraying the heated slurry at temperature above 100°C into a spray-drying tower;
   (c) spray-drying the slurry to form a spray-dried powder.

2. A process according to claim 1, wherein the aqueous slurry is heated to a temperature at least 123°C.

3. A process according to any preceding claim, wherein the heated slurry is sprayed at a temperature of at least 123°C into the spray-drying tower.

4. A process according to any preceding claim, wherein the heated slurry is sprayed at a pressure of at least $4x10^6$ Pa into the spray-drying tower.

5. A process according to any preceding claim, wherein the slurry is heated by the addition of saturated steam.

6. A process according to any preceding claim, wherein the slurry is heated by a chemical or nuclear exothermic reaction.

7. A process according to any preceding claim, wherein the slurry is heated by solar energy.

8. A process according to any preceding claim, wherein the spray-dried powder is contacted with non-ionic detersive surfactant.

Europäisches Patentamt
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EUROPEAN SEARCH REPORT

Application Number
EP 08 15 9034

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 844 969 A (GRIFFITHS J ET AL) 29 October 1974 (1974-10-29)	1-8	INV. C11D11/02
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TECHNICAL FIELDS SEARCHED (IPC)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	17 December 2008	Culmann, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 15 9034

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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17-12-2008

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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- US 6020303 A **[0015]**
- US 6060443 A **[0015]**

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AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the twenty-third day of August, 1948, under Section 26 of the Patents and Designs Acts, 1907 to 1946.

PATENT SPECIFICATION 575,118

Application Date: June 28, 1944. No. 12285/44.

Complete Specification Left: June 5, 1945.

Complete Specification Accepted: Feb. 4, 1946.

PROVISIONAL SPECIFICATION

Improvements in or relating to Methods of and Means for Preparing Concentrated Liquid or Solid Extracts of Tea or Coffee

I, JAMES ARTHUR REAVELL, a British subject, of 5, Grosvenor Gardens, London, S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to methods of and means for preparing concentrated liquid or solid extracts of tea or coffee.

It is known that coffee or tea may be extracted with water and that the aqueous extract or infusion can be evaporated to produce a concentrated liquid extract. It is also known that such liquid extracts may be dried, for example, by spray drying to produce a dry extract in the form of a soluble powder. In either case, because of the volatile nature of the aromatic constituents, much of the original aroma or bouquet is often lost during the extraction, evaporation or drying operations.

The chief object of the present invention is to provide an improved and convenient method of producing concentrated liquid extracts or dry powders from tea or coffee whereby a large percentage of the original aroma, bouquet or flavouring constituents is retained so that a beverage with a taste, flavour or aroma bearing a close resemblance to that of a freshly prepared beverage may be produced therefrom.

In accordance with the invention an aqueous infusion of tea or coffee is prepared in a closed extractor so that the aroma or flavouring ingredients are retained in the infusion and the latter is thereafter evaporated or concentrated under such conditions that the volatile aromatic or flavouring constituents are distilled off and separately condensed for return or addition at a later stage to the extract or final product.

In instances in which liquid extracts are being produced, the separated aromatic or flavouring bodies are returned to the concentrated liquor with or without fractionation to reduce their volume and, in instances in which dried extracts are required, the concentrated extract may be dried, for example, in a spray drier and the separated aromatic or flavouring bodies may be fractionated to small bulk and then adsorbed into the dried powder. If desired, when producing coffee powders, a soluble carbohydrate such as glucose or lactose may be added to the concentrate before spray drying, it having been found that hereby the dried powder is rendered less hygroscopic. The amount of carbohydrate added preferably corresponds to between one tenth to equal weight of the pure coffee powder.

In carrying the invention into effect according to one convenient mode, a hot extraction of the tea or coffee is prepared in a closed extractor and the extract as it is run off is passed through a water jacketted conduit or other cooling means so that the temperature of the extract is reduced to a value below that at which the aromatic or flavouring bodies are noticeably volatile. The cooled extract thus obtained is then evaporated and at this stage the aromatic or flavouring bodies are distilled off and separated. Alternatively, instead of cooling the extract, it may be passed into a vessel or apparatus maintained under vacuum so that the volatile aromatic or flavouring bodies are flashed off immediately and condensed

[Price 1/-]

Price 4s 6d.

Price 4s 6d.

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separately, the remainder of the extract being then concentrated.

The initial aqueous extract or infusion of tea or coffee may be produced in any desired manner. For example, a batch of fresh tea or coffee may be leached with hot weak extract (at or near boiling point) from a previous extraction to produce a strong extract and the coffee or tea may then be further extracted with still weaker extract and finally with hot water. Other known methods such as percolation and recirculation of liquor may be used.

As regards the evaporation, this is preferably carried out in an evaporator operating on the climbing film principle and equipped with means for effecting the removal of the aromatic constituents. Thus, for example, referring to the accompanying drawing which illustrates one form of apparatus that may be used, *a* indicates a feed tank for the aqueous extract to be concentrated, *b* indicates a heater by which the liquor is subjected to a preliminary heating and *c* and *d* indicate a still by which the volatile aromatic constituents obtained as a result of the preliminary heating are distilled off. The preliminary heater may conveniently consist of a tube a^1 extending longitudinally through another tube or casing a^2 arranged so that steam may be delivered to the space between the outer surface of the inner tube and the inner surface of the outer tube and the still may be similarly formed so that its inner tube forms a continuation of the inner tube of the heater. As will be seen, the volatile constituents are passed from the vessel or separator *d* into a condenser *e* and the condensate consisting of the flavour aroma imparting ingredients is led away into a receiver *f*. On the other hand, the liquid obtained from the separator *d* is led by means of a conduit *g*, from the bottom of the separator to the lower end of the evaporator or concentrator *h* which constitutes the evaporating apparatus proper.

The said evaporator is of the continuous type and operates on the "Kestner" climbing film principle having two or three evaporating stages. For example, the arrangement may be such that the liquor and vapours derived from the first stage are led into a separator *m* from which the liquor is led by a conduit *n* back into the evaporator and thence into a second separator *o*. The liquor obtained from the latter may then be returned to the evaporator so that the liquor rises up the evaporator and gives off its vapour when passing into a third separator *p* from which the concentrated liquid passes to a receiver *q*. Thus each evaporating stage is provided with a separate separator. Preferably, a common vacuum pipe *r* leading to a suitable form of condenser and vacuum system is connected to all of the separators as shown.

As mentioned above, the aroma or flavouring ingredients are eventually returned or added to the extract or final product.

The following examples illustrate how the invention may be carried into effect:—

EXAMPLE 1.

About 50 lbs. of coffee are treated in a closed extractor to yield about 156 lbs. of an aqueous extract having a specific gravity of 1.025 and containing approximately 4.8% solids and the hot extract is cooled as it leaves the extractor to a temperature of about 50°C. Such extract is then evaporated in a climbing film evaporator, the aromatic or flavouring bodies or esters being distilled off and condensed separately and amounting in all to 1300 ml. of aqueous solution. In this manner, a main body of concentrated extract amounting to 34 lbs. having a specific gravity of 1.10 and containing approximately 22% solids, is obtained and, after adding thereto the aqueous solution of aromatic bodies, approximately 37 lbs. of concentrated extract containing 20% solids has been produced and it has been found that when this concentrate is reconstituted with hot water there is produced a beverage having an extremely close resemblance to fresh coffee.

EXAMPLE 2.

About 50 lbs. of coffee are treated as in Example 1 to yield after evaporation about 35 lbs. of concentrate containing 22.5% solids and 1200 ml. aqueous solution of aromatic bodies. The concentrate is then spray dried in a spray drier having a centrifugal type of atomiser and supplied with hot air which is supplied at 160°C. and leaves the dryer at 75°C. In this manner, 7¾ lbs. of dry coffee powder is produced. The 1200 ml. of aqueous aromatic bodies is reduced by fractional distillation to a volume of 35 ml. and thereafter the powder and the reduced volume of aromatic bodies are both placed in a closed container and left for a period of about 24 hours when it will be found that practically the whole of the aromatic bodies has become adsorbed into the powder.

EXAMPLE 3.

About 50 lbs. of coffee are extracted as in Example 2 and to the 35 lbs. of concentrate 1.65 lbs. of a carbohydrate such as lactose are added before carrying out the spray drying operation. In this manner, 8.4 lbs. of dried coffee powder containing dried lactose is obtained and into this is

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adsorbed 30 ml. of reduced volume of aromatic bodies as before. It has been found that the addition of lactose is advantageous in that it renders the dried powder less hygroscopic.

EXAMPLE 4.

About 25 lbs. of fresh tea leaves are treated in a closed extractor to yield about 120 lbs. of an aqueous extract having a specific gravity of 1.0175 and containing approximately 5% solids. The extract is cooled as it leaves the extractor to about 50°C. and it is then evaporated in a climbing film evaporator, and the aqueous solution of the aromatic constituents is recovered and condensed separately. In this manner, 36 lbs. of concentrate is obtained and this is then dried in a spray drier employing hot air as the heating medium, the air being supplied at a temperature of 155°C. and leaving the drier at 75°C. 6.0 lbs. of dried powder is thus obtained and the aqueous condensate of aromatic bodies reduced in volume by fractional distillation to 30 ml. is then absorbed into the powder by standing the two in a closed container for a period of about 36 hours.

EXAMPLE 5.

About 25 lbs. of fresh tea leaves are treated in a closed extractor to yield about 120 lbs. of an aqueous extract having a specific gravity of 1.0175 and containing approximately 5% solids. The extract leaving the extractor at about 85°C. is passed into a vessel maintained under vacuum of 15" mercury with the result that 1000 ml. of aqueous solution of aromatic constituents is separated and condensed. The remaining hot concentrate is evaporated in a climbing film evaporator to produce 45 lbs. of concentrate containing 13.3% solids. This concentrate is then dried as in Example 4 and into the dried powder is absorbed the aromatic constituents after reduction in volume by fractional distillation as in Example 4.

Dated this 28th day of June, 1944.

ARTHUR W. PARFITT,
Chartered Patent Agent,
Stafford House, Norfolk Street,
Strand, London, W.C.2.

COMPLETE SPECIFICATION

Improvements in or relating to Methods of and Means for Preparing Concentrated Liquid or Solid Extracts of Tea or Coffee

I, JAMES ARTHUR REAVELL, a British subject, of 5, Grosvenor Gardens, London, S.W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to methods of and means for preparing concentrated liquid or solid extracts of tea or coffee.

It is known that coffee or tea may be extracted with water and that the aqueous extract or infusion can be evaporated to produce a concentrated liquid extract. It is also known that such liquid extracts may be dried, for example, by spray drying to produce a dry extract in the form of a soluble powder. In either case, because of the volatile natnre of the aromatic constituents, much of the original aroma or bouquet is often lost during the extraction, evaporation or drying operations and in order to overcome this difficulty in the production of liquid coffee concentrate it has previously been proposed to trap or condense the volatile aromatic constituents which pass off with the evaporated water during the concentration of the liquid coffee extract and to return the said trapped and condensed aromatic constituents by one means or another to the concentrate from which the said constituents have been distilled.

I am aware of a prior suggestion for carrying the above mentioned prior proposal into effect by a method of and apparatus for batch extraction of liquid coffee concentrate whereby a dilute coffee extract obtained from the secondary brewing of coffee grounds is boiled in a distillation tank until sufficiently concentrated and the steam and vapours given off from the boiling dilute extract while carrying the volatile aromatic constituents of the extract are trapped and condensed and the highly aqueous condensate is returned to the cooled concentrate and mixed therewith.

The chief object of the present invention is to provide an improved and convenient method of producing concentrated liquid extracts or dry powders from tea or coffee whereby a large percentage of the original aroma, bouquet or flavouring constituents is retained so that a beverage with a taste, flavour or aroma bearing a close resemblance to that of a freshly prepared beverage may be produced therefrom.

In accordance with the invention an

aqueous infusion of tea or coffee is prepared in a closed extractor so that the aroma or flavouring ingredients are retained in the infusion and the latter is thereafter evaporated or concentrated in a continuous heating and condensing system wherein the infusion is passed through a preliminary heating or evaporation stage in order to distil off and separate the volatile aromatic or flavouring constituents from the bulk of the infusion which is thereafter evaporated or concentrated at a separate heating stage or evaporation stage proper, and wherein the separated volatile or flavouring constituents are condensed for return or addition at a later stage to the extract or final product.

In instances in which liquid extracts are being produced, the separated aromatic or flavouring bodies are returned to the concentrated liquor with or without fractionation to reduce their volume and, in instances in which dried extracts are required, the concentrated extract may be dried, for example, in a spray drier and the separated aromatic or flavouring bodies may be fractionated to small bulk and then absorbed into the dried powder. If desired, a soluble carbohydrate such as glucose or lactose may be added to the concentrate before spray drying, it having been found that thereby the dried powder is rendered less hygroscopic. Alternatively, a soluble carbohydrate may be added or mixed with the fresh tea or coffee before extraction or the said carbo-hydrate may be added to the water or weak extract from a previous extraction. For example, when producing coffee powder, it has been found that the addition of a carbo-hydrate such as glucose or lactose renders the product less hygroscopic. The amount of carbohydrate added preferably corresponds to between one-tenth to equal weight of the pure coffee powder. Reduction of hygroscopicity improves or adds to the value of the dried powders of this nature since amongst other things it greatly increases the keeping qualities of the powders.

In carrying the invention into effect according to one convenient mode, a hot extraction of the tea or coffee is prepared in a closed extractor and the extract as it is run off is passed through a water jacketted conduit or other cooling means so that the temperature of the extract is reduced to a value below that at which the aromatic or flavouring bodies are noticeably volatile. The cooled extract thus obtained is thereupon evaporated and condensed in the continuous evaporating system hereinafter described and at the initial stage the aromatic or flavouring bodies are distilled off and separated. Alternatively, if it is not desired to store the extract and such extract is to be passed at once to the said continuous evaporating and condensing system, it is passed first at an appropriate temperature into a vessel or apparatus maintained under vacuum so that the volatile aromatic or flavouring bodies are flashed off immediately and condensed separately, the remainder of the extract being then concentrated in the said continuous system.

The initial aqueous extract or infusion of tea or coffee may be produced in any desired manner. For example, a batch of fresh tea or coffee may be leached with hot weak extract (at or near boiling point) from a previous extraction to produce a strong extract and the coffee or tea may then be further extracted with still weaker extract and finally with hot water. Other known methods such as percolation and recirculation of liquor may be used.

As regards the evaporation, this is preferably carried out in an evaporator operating on the climbing film principle and equipped with means for effecting the removal of the aromatic constituents. Thus, for example, referring to the drawing which accompanies the Provisional Specification, and which illustrates one form of apparatus that may be used, *a* indicates a feed tank for the aqueous extract to be concentrated, *b* indicates a heater by which the liquor is subjected to a preliminary heating and *c* and *d* indicate a still by which the volatile aromatic constituents obtained as a result of the preliminary heating are distilled off. The preliminary heater may conveniently consist of a tube a^1 extending longitudinally through another tube or casing a^2 arranged so that steam may be delivered to the space between the outer surface of the inner tube and the inner surface of the outer tube and the still may be similarly formed so that its inner tube forms a continuation of the inner tube of the heater. As will be seen, the volatile constituents are passed from the vessel or separator *d* into a condenser *e* and the condensate consisting of the flavour or aroma imparting ingredients is led away into a receiver *f*. On the other hand, the liquid obtained from the separator *d* is led by means of a conduit *g*, from the bottom of the separator to the lower end of the evaporator or concentrator *h* which constitutes the evaporating apparatus proper.

The said evaporator is of the continuous type and operates on the "Kestner" climbing film principle having two or three evaporating stages. For example, the arrangement may be such that the

liquor and vapours derived from the first stage are led into a separator *m* from which the liquor is led by a conduit *k* back into the evaporator and thence into a second separator *o*. The liquor obtained from the latter may then be returned to the evaporator so that the liquor rises up the evaporator and gives off its vapour when passing into a third separator *p* from which the concentrated liquid passes to a receiver *q*. Thus each evaporating stage is provided with a separate separator. Preferably, a common vacuum pipe *k* leading to a suitable form of condenser and vacuum system is connected to all of the separators as shown.

As mentioned above, the aroma or flavouring ingredients are eventually returned or added to the extract or final product.

The following examples illustrate how the invention may be carried into effect:—

EXAMPLE 1.

About 50 lbs. of coffee are treated to yield after evaporation about 35 lbs. of concentrate containing 22.5% solids and 1200 ml. aqueous solution of aromatic bodies. The concentrate is then spray dried in a spray drier having a centrifugal type of atomiser and supplied with hot air which is supplied at 160°C. and leaves the drier at 75°C. In this manner 7¾ lbs. of dry coffee powder is produced. The 1200 ml. of aqueous aromatic bodies is reduced by fractional distillation to a volume of 35 ml. and thereafter the powder and the reduced volume of aromatic bodies are both placed in a closed container and left for a period of about 24 hours when it will be found that practically the whole of the aromatic bodies has become absorbed into the powder.

EXAMPLE 2.

About 50 lbs. of coffee are extracted as in Example 1 and to the 35 lbs. of concentrate 1.65 lbs. of carbohydrate such as lactose are added before carrying out the spray drying operation. In this manner, 4 lbs. of dried coffee powder containing dried lactose is obtained and into this is absorbed 30 ml. of reduced volume of aromatic bodies as before. It has been found that the addition of lactose is advantageous in that it renders the dried powder less hygroscopic and that, in consequence, the keeping qualities of the powder are very considerably increased.

EXAMPLE 3.

About 50 lbs. of coffee are extracted as in Example 1 but, in this instance, about 1.65 lbs. of carbohydrate such as lactose are added to the coffee, prior to concentration, either as a solid carbohydrate or as a solution, before the addition of the water or weak extract from a previous extraction. After extraction, the concentrate is spray dried as before. In this manner 8.4 lbs. of dried coffee powder containing dried carbohydrate and having enhanced keeping qualities are obtained and into this is absorbed 30 ml. of reduced volume of aromatic bodies as already described.

EXAMPLE 4.

About 50 lbs. of coffee are extracted as in Example 1, in this instance, about 1.6 lbs. of carbohydrate such as lactose are added, not to the coffee or its extract as such but to the water or weak extraction from a previous extraction used for the extraction of this batch of coffee. In this manner also, about 8.4 lbs. of dried coffee powder containing dried carbohydrate and having enhanced keeping qualities may be obtained and into the same there is absorbed 30 ml. of reduced volume of aromatic bodies as already described.

EXAMPLE 5.

About 25 lbs. of fresh tea leaves are treated in a closed extractor to yield about 120 lbs. of an aqueous extract having a specific gravity of 1.0175 and containing approximately 5% solids. The extract leaving the extractor at about 85°C. is passed into a vessel maintained under vacuum of 15" mercury with the result that 1000 ml. of aqueous solution of aromatic constituents is separated and condensed. The remaining hot concentrate is evaporated in a climbing film evaporator to produce 45 lbs. of concentrate containing 13.3% solids. This concentrate is then dried and into the dried powder is absorbed the aromatic constituents after reduction in volume by fractional distillation.

EXAMPLE 6.

About 25 lbs. of fresh tea leaves are treated in a closed extractor as is described in Example 5 but, in this instance, about 0.75 lbs. of carbohydrate are added to the water or weak extract from a previous extraction to be used for obtaining the present extract.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A method of preparing a concentrated liquid extract of tea or coffee wherein an aqueous infusion of tea or coffee is prepared in a closed extractor so that the aroma or flavouring ingredients are retained in the infusion, the latter is thereafter evaporated or concentrated in a continuous evaporating and condensing system wherein the infusion is passed through a preliminary heating or evapor-

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ation stage in order to distil off and separate the volatile aromatic or flavouring constituents from the bulk of the infusion which is thereafter concentrated by evaporation while passing through a separate heating stage or evaporation stage proper, and wherein the separated volatile or flavouring constituents are condensed and (with or without fractionation to reduce the volume thereof) are returned to the concentrated liquor.

2. A method of preparing a dry powder extract of tea or coffee wherein an aqueous infusion of tea or coffee is prepared in a closed extractor so that the aroma or flavouring ingredients are retained in the infusion, the latter is thereafter evaporated or concentrated in a continuous evaporating and condensing system wherein the infusion is passed through a preliminary heating or evaporation stage in order to distil off and separate the aromatic or flavouring constituents from the bulk of the infusion which is thereafter concentrated by evaporation while passing through a separate heating stage or evaporation stage proper and then dried to powder form and wherein the separated volatile or flavouring constituents are condensed and reduced in volume by fractionation and returned by adsorption into the dried powder.

3. A method of preparing a concentrated extract of tea or coffee having the features claimed in either of the preceding claims wherein the evaporation is carried out in a climbing film evaporator.

4. A method of preparing a dry powder extract as claimed in claim 2 wherein a soluble carbohydrate such as glucose or lactose is added to the concentrate before it is subjected to the drying treatment.

5. A method of preparing a dry powder extract as claimed in claim 2 wherein a soluble carbohydrate such as glucose or lactose is added to the extracting solution to be used for obtaining the aqueous infusion of the tea or coffee.

6. A method as claimed in claim 4 or 5 in which the amount of carbohydrate added corresponds to between one tenth to equal weight of the pure tea or coffee powder.

7. Means for preparing concentrated extracts of tea or coffee according to the method claimed in any of the preceding claims comprising a closed extractor and means whereby an aqueous infusion obtained from an extractor is caused to travel in an upward direction through an evaporating apparatus operating on the climbing film principle and equipped with means for removing and separately condensing the volatile aromatic constituents.

8. Means as claimed in claim 7 wherein means is provided for cooling the extract as it leaves the extractor and passes to the evaporating apparatus.

9. Means for carrying out the method claimed in any of the preceding claims 1 to 6 comprising a closed extractor, means for conducting the hot extract from the extractor to a receiver held under vacuum so that the volatile aromatic constituents are continuously flashed off and condensed separately and means whereby the remaining hot concentrate is continuously evaporated in an evaporator operating on the climbing film principle.

10. Means as claimed in claim 7, 8 or 9, wherein the evaporating apparatus has a plurality of evaporating stages each provided with a separate separator and a common vacuum pipe connected to both or all of the separators.

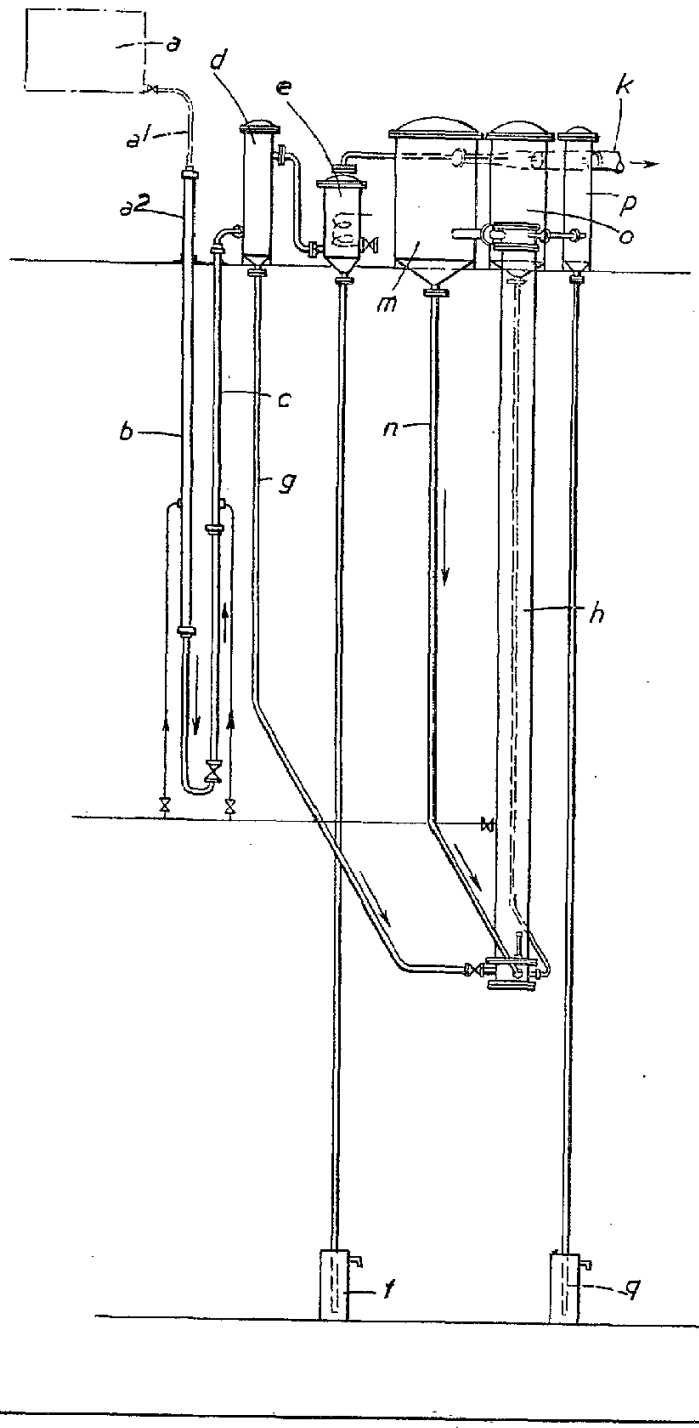
11. A method of preparing concentrated liquid or solid extracts of tea and coffee substantially as hereinbefore described.

12. Means for preparing concentrated extracts of tea or coffee substantially as hereinbefore described with reference to the accompanying drawing.

Dated this 5th day of June, 1945.
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[This Drawing is a reproduction of the Original on a reduced scale.]

H.M.S.O.(Ty. P.)

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Drying Liquid Materials Containing Dissolved and/or Suspended Solids

We, Birs Beteiligungs- Und Verwaltungsgesellschaft A.G., a Swiss Body Corporate of Elisabethenstrasse 15, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a counter-current drying process wherein a fine dispersion of liquid material containing dissolved and/or suspended solids is contacted with air or other gaseous drying medium, at a temperature in the range of 0 to 60°C., depending on the kind of goods, preferably at a constant temperature of 15 to 18° or 25 to 30°C., in a drying tower. This so-called cold-or cool-air-drying process has the object of preventing the denaturation of the starting material and especially of obtaining an easily soluble end product. Owing to the low temperature of the drying air the duration of the material in the drying tower is relatively long, its volume is considerable and, as a consequence, considerable quantities of drying air are required. Such a process, which is especially applicable for mass products of high value, has exceptional economic prospects if it operates with the smallest possible heat consumption. This is, however, in the first place, possible only if heat recuperation is effected.

Drying towers useful for the practice of this invention preferably have height in the range of 50 m. to 200 m., tower heights of about 70 m. having been found most useful for most purposes.

A minimum of operating units are required for conditioning the drying air, since a considerable part of these units can be structurally united with the drying tower. By using the tower walls for heat recovery and by placing the dehumidification housing into the drying air and heating cycle, a constant entry temperature of the drying air into the tower is maintained over each cycle of dehumidification and regeneration of the air, without heating or cooling of the drying air by supplementary means, or with a minimum thereof. This temperature equilibrium is obtained inside the drying housing in multiple steps. For part of the time, the drying air is additionally heated in the drying tower from the walls of the tower so that the air keeps its entry temperature while streaming upwardly in the tower and thus maintains its drying power almost until it reaches the region where the liquid material is released.

The dehumidification of the drying air is effected with the aid of adsorption media, such as silica gel or molecular sieves and experience has shown that a packing of such adsorption media may remove water from the air passed therethrough for about 5 to 6 hours. This must then be followed by a regeneration cycle of about equal duration when hot air of constant temperature is passed through the adsorption medium packing, the temperature of the regenerating air ranging between about 150°C. and 300°C., depending on the adsorption medium.

The cold or cool air drying requires a constant supply of dehumidified air of a temperature of about 25°C. to 30°C., for instance, for introduction into the drying tower. Air at about 160°C. is used for regenerating the dehumidifying packing if silica gel is used for this purpose. Thus, the invention provides improved means for conditioning the air in this manner with a minimum of servicing.

This is accomplished in accordance with the present invention by passing the fresh

[1

air through a chamber defined by the outer wall of the drying tower and a heat-storing intermediate wall between the outer and inner walls of the tower, while the dehumidified fresh air is passed through the chamber defined by the inner tower wall and the intermediate wall, which has an inwardly facing heat-insulating lining, after it has been conducted through the dehumidifying adsorption medium and before it is introduced into the drying tower. If additional cooling of the walls of the first named chamber is required, the fresh air for regenerating the adsorption medium may also be passed through the first-named chamber on its way to a heat-storage device in the regenerating cycle.

Further according to the invention there is provided a drying tower using dehumidified atmospheric air as a drying medium, comprising a heat-storing jacket surrounding the tower, said jacket being defined by an outer and an inner wall of heat-storing material, an intermediate wall of a heat-storing material in said jacket, said intermediate wall dividing the jacket into two chambers adjacent the outer and inner wall, respectively and dividing each of said chambers into a plurality of cells extending along said walls, and a heat-insulating layer on said intermediate wall facing the inner tower wall.

To obtain a drying air of constant temperature over a period of 24 hours, use is made of two facts, i.e. the temperature difference of the atmospheric air between night and day time, on the one hand, and the rise of adsorption medium temperature during the 5 to 6 hours dehumidifying cycle from about 15 to 20°C. to about 40 to 50°C. If the fresh air is passed through the outer chamber of the double wall or jacket of the drying tower during the night, the heat-storing intermediate wall in the jacket will be cooled, together with the heat-storing outer wall of tower, to such a degree that the fresh air conducted to the adsorption medium will never exceed a maximum temperature of about 20°C. during the entire day. The lower the temperature of the air passing through the adsorption medium packing, the higher the dehumidification efficiency of the packing. In the initial time period of dehumidification, the dried air leaves the packing with an average temperature of about 25°C. In the preceding cycle corresponding to the final time period of dehumidification, the dried air left the adsorption medium at a temperature of about 50°C. and caused the inner wall of the drying tower jacket to be heated to an average temperature of 45°C., as it passed through the inner jacket chamber before introduction into the drying tower. Heat exchange accordingly causes the initially dehumidified air to be heated to 35°C. during its passage through the inner jacket chamber on its way to the drying tower, at which temperature it then enters the interior of the tower. In the second period of dehumidification, the dried air leaves the packing with an average temperature of about 35°C. and this rises to 45°C. or so in the final dehumidification period. The warmer air raises the temperature of the previously cooled tower wall so that heat exchange continues to keep the temperature of the dehumidified air entering the drying tower at about 35°C. This cycle is repeated as additional fresh air is passed through a second adsorption medium packing which has, meanwhile, been regenerated.

Temperature control may be obtained by imparting a zig-zag configuration to the intermediate wall in the drying tower jacket, which increases its heat-storage capacity and also sub-divides the space between the outer and inner tower walls into individual cells. The heat exchange may then be controlled by suitable control of the passage the amount of air streams into the individual cells. Thus, a variety of drying air temperatures may be obtained independently of the temperature of the atmospheric air, in addition to the temperature of 35°C. given hereinabove by way of example. In case of extreme climatic conditions or specially low drying air temperatures required for certain materials, for instance, 18°C. for drying butter, special heat exchangers for cooling or heating the fresh air may be positioned in the fresh air conduits ahead of the adsorption medium or the inlet into the drying tower. In most instances, however, it is possible to dispense with such special heat exchangers or to operate the same only for short periods of time at certain points of the cycle.

Since the temperature of the dehumidification packing rises at the end of the dehumidification and regeneration cycles, suitable thermocouples may be used for automatically switching the packings from the dehumidification to the regeneration cycle, and vice versa. If desired, the entry temperature of the drying gas into the drying tower maybe used to initiate this switching a little sooner, particularly if the latter temperature is also used to direct the drying air suitably through the individual jacket cells and to control its throughput to obtain the desired drying gas temperature. If a thermostat indicates this desired temperature to be exceeded, it may then automatically switch the gas stream through a freshly regenerated adsorption medium while causing regeneration of the exhausted medium. The entire air circulation through the drying plant may be effected by fans

mounted in the fresh air inlet openings of the outer wall of the drying tower.

The invention is illustrated by way of example in the accompanying drawings which show a structural embodiment of the plant for conditioning the drying air in the indicated manner, Fig. 1 being a vertical section of the plant and Fig. 2 showing a horizontal section thereof. To facilitate a schematic showing of the conduits, the dehumidifier elements 2*a*, 2*b*, and the heat-storage devices 3*a*, 3*b*, are shown in Fig. 1 one behind the other, while they are illustrated adjacent one another in Fig. 2. In practice, they are arranged only at one of the two locations. Heat exchangers 6 and 7 also are positioned at the same location.

The drying air enters the drying tower 1 at inlet opening 9 and passes upwardly to outlet opening 11. The liquid material distributing means (not shown) is mounted in the tower below the drying gas outlet opening. The dried material, a porous solid, is removed at the base of the tower. The tower, which may have circular or rectangular walls, is surrounded by a jacket formed by an inner and outer tower wall defining a space therebetween. This space is divided into outer cells 4 and inner cells 5 by an intermediate zig-zag wall which has a heat-insulating lining facing the interior of the tower. It is preferred to make all the walls of cement which has a considerable heat-storing capacity. For a drying plant designed to dry about 5000 litres of liquid starting material per hour in a drying tower of 70 m. height, about 5000 to 6000 tons of cement will be needed to build the jacket walls with its dividing wall.

The fresh air for drying as well as adsorption medium regeneration is passed into the plant from the atmosphere through the outer cells 4 of the tower jacket. If desired, the air may be led up and down the cells several times before leaving the jackets. For instance, it may be blown into the cells 4 of one side wall of the tower by eight fans mounted in front of suitable inlet openings 8 in the wall. It may then be directed, for instance, from the lower cells of the one wall into the outer cells 4 of the two adjacent walls, passing upwardly through these cells and being conducted by suitable conduits from the upper cells into the outer cells of the adjacent wall opposite to the first-named wall, whence the air is led through openings in the lower portion of the latter wall into a header.

As shown in Fig. 1, the header is subdivided into two branch conduits. In one of the operating cycles, the fresh air, which has been pre-heated or pre-cooled by passage through jacket cells 4, is led through the upper branch conduit into a regenerated adsorption medium packing 2*a* consisting of two vertical packings arranged in parallel. The other portion of the pre-heated fresh air is conducted into a heat storage device 3*a*. The entry valve of the lower branch conduit then remains closed. In the following operating cycle, a portion of the fresh air coming from cells 4 is conducted by the lower branch conduit to adsorption medium packing 2*b* which is similar in structure to packing 2*a*. The other portion of the fresh air is then led from the lower branch conduit to heat storage device 3*b*. At this cycle, the entry valve of the upper branch circuit remains closed.

Depending on the cycle, the dehumidified air coming from packing 2*a* or 2*b* is conducted to the inner cells 5 of the tower jacket and is led up and down these cells in a manner similar to that described in connection with the passage of the fresh air through cells 4. Finally, the dehumidified and conditioned drying air is introduced into the tower through opening 9.

The fresh air which is further heated in the heat storage device 3*a* or 3*b* is heated further in the chimney, which is constructed at a heat exchanger 6, by the exhaust gases from the firing system of another heat exchanger 7 and is finally brought to the required regeneration temperature in this heat exchanger 7. This hot air is then directed to the adsorption medium packing requiring regeneration, whence it is passed into one of heat storage devices 3*a* or 3*b* to heat the same. The regenerating air then passes from the heat storage device into the atmosphere through flue 10. The inlet openings for cells 4, which admit the fresh air thereto, and for cells 5, admitting the dehimidified and conditioned drying air, are provided with suitable filters.

If the temperature of the adsorption packing used for dehumidifying the air exceeds a predetermined value, for instance 50°C., a thermosensitive relay may automatically operate suitable valves in the air conduits to direct the fresh air to a previously regenerated adsorption packing and to direct the regenerating air to the exhausted packing. The control of the next cycle may then be taken over by a thermostat in the regenerated packing. However, the cycle control may also be effected in an obvious manner by a thermostat in the conduit directing the conditioned air to cells 5.

By using a tower wall jacket as heat storage and balancing device, it is possible to equalize the air temperatures so as to obtain a drying air of nearly constant temperature throughout the operation of the tower. Since the atmospheric air is first led through outer jacket cells 4, its temperature may be raised or lowered sufficiently on its way to the adsorption packing so that the conditioned and dehumidified air

will never drop below a given temperature, for instance 25 to 30°C., at its entrance into the tower. Temperature control may be achieved by creating zones of different temperatures in the tower jacket. For instance, the fresh air supply fans, which may be eight or nine in number, for instance, may each supply a separated air conduit leading to the header so that, depending on the fan speed and the corresponding air throughput of each fan, the air entering the adsorption packing from each conduit has a different temperature. In a similar manner, the drying air may be prevented from reaching a temperature higher than desired by conducting the air on its way to the tower through more or fewer cooled cells 5. Excess air temperature toward the end of the dehumidifying cycle may also be avoided by switching prematurely to the subsequent cycle as soon as the temperature reaches a certain point if it would be impossible to change the air path through the jacket cells. This switch may be automatically effected by a thermostat at inlet opening 9.

Since the time period during which drying air is introduced into the tower at a temperature substantially exceeding the desired temperature level is relatively short in each cycle, the inner wall of the tower jacket will be maintained at substantially constant temperature. This may be accomplished by suitably dimensioning the wall thicknesses. Furthermore, additional control may be obtained, if desired, by lining the outwardly facing surface of the intermediate jacket wall with an insulating layer in some of the jacket cells. Heat storage is effected primarily in the zig-zag intermediate wall in the tower jacket. It is also possible to make the volume of cells 4 and 5 different, for instance to make the cells 5 larger than cells 4. The amount of air passing through cells 4 may be one and a half or two times that passing through cells 5, depending on the ratio of drying air to regenerating air, so that the cool night air may be used to an increased extent for cooling the heat exchangers.

As indicated hereinabove, the adsorption medium regenerating air is not led through cells 5 but is passed into the atmosphere at 10. The rising drying air tends to decrease in temperature from the bottom to the top of the tower and if desired, the jacket space may be sub-divided by horizontal partition walls so that the inner wall of the tower jacket will be kept at different temperatures at different levels.

Some water will be removed from the fresh air by condensation as it passes through the outer jacket cells and a suitable water outlet is provided at the bottom of cells 4 in the jacket. This condensation from the fresh air occurs only at periods when hotter daytime air is passed through the cells 4 after prior cooling of the walls thereof by the cold night air.

WHAT WE CLAIM IS :—

1. A counter-current drying process wherein a fine dispersion of liquid material containing dissolved and/or suspended solids is contacted with air or other gaseous drying medium at a temperature of about 0 to 60°C., in a drying tower, comprising the steps of conducting atmospheric air through a first chamber of a jacket made of heat-storing material surrounding the tower, said jacket being defined by an outer wall and an inner wall of the tower and said first chamber being defined by the outer wall and an intermediate wall in the jacket, passing the air from said first chamber into and through a water adsorption medium to dehumidify the air, and passing the dehumidified air through a second jacket chamber defined by said intermediate wall and the inner tower wall whence the dehumidified air is passed into the tower, the surface of the intermediate wall facing the inner tower wall being heat insulated.

2. A drying process as claimed in Claim 1, further comprising the steps of passing a portion of the air from said first jacket chamber into a heat exchanger, heating the air therein and passing the heated air through another water adsorption medium for regenerating the same.

3. A drying process as claimed in Claim 1, further comprising the steps of continuously measuring the temperature of the dehumidified air entering the tower and controlling the amount and path of the atmospheric air passing through the first and second chambers of the jacket in response to the measured temperature.

4. A drying process as claimed in Claim 2, further comprising the steps of continuously measuring the temperature of the dehumidified air entering the tower and controlling the flow of atmospheric air from said first chamber alternately between the one and the other water adsorption medium in response to the measured temperature whereby one of the adsorption media is used to dehumidify the atmospheric air while the other one is being regenerated.

5. A drying process as claimed in Claim 2, further comprising the steps of blowing the atmospheric air into the first jacket chamber, and passing said air portion through a succession of heat-storing and heat exchanging means on its way to the adsorption medium to be regenerated.

6. A drying tower using dehumidified atmospheric air as a drying medium, comprising a heat-storing jacket surrounding the tower, said jacket being defined by an outer and an inner wall of heat-storing

material in said jacket, said intermediate wall dividing the jacket into two chambers adjacent the outer and inner wall, respectively and dividing each of said chambers into a plurality of cells extending along said walls, and a heat-insulating layer on said intermediate wall facing the inner tower wall.

7. A drying tower as claimed in Claim 6, wherein the thickness of the intermediate wall exceeds that of the inner and outer tower walls.

8. A drying tower as claimed in Claim 6, further comprising a heat-insulating layer on said intermediate wall facing the outer tower wall in some of said cells.

9. A drying tower as claimed in Claim 6, further comprising air conduit means interconnecting groups of said cells.

10. A drying tower as claimed in Claim 9, comprising a fan supplying atmospheric air to each of said cell groups.

11. A counter-current drying process substantially as described herein with reference to the accompanying drawings.

12. A drying tower constructed and arranged substantially as described herein with reference to the accompanying drawings.

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1,015,599 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

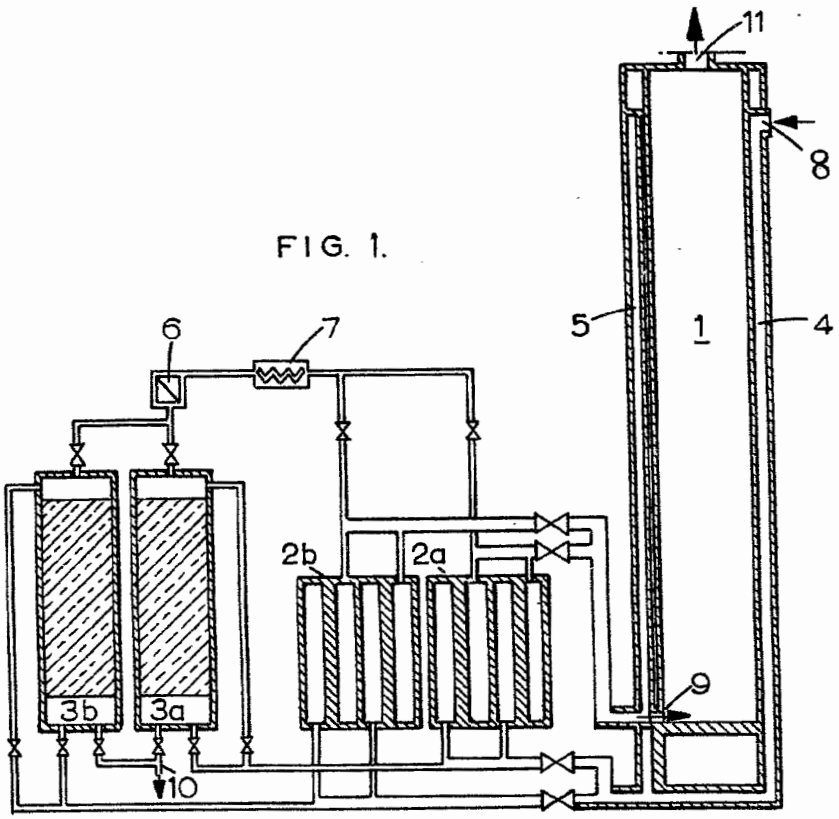


FIG. 1.

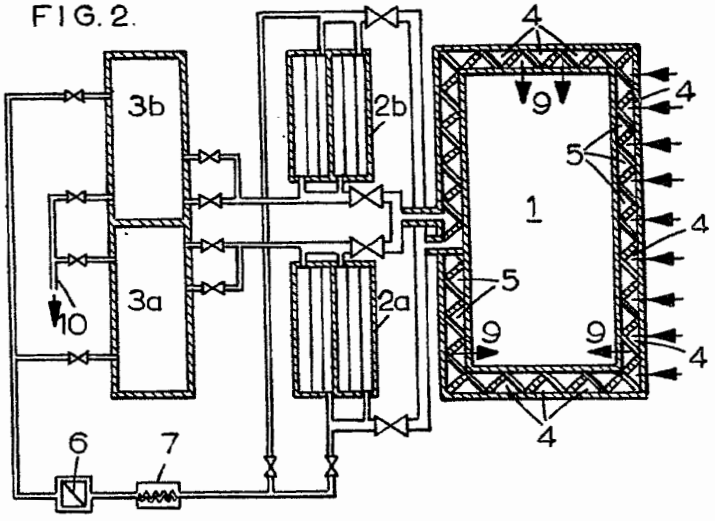


FIG. 2.

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(54) Abstract Title
Spray-drying a material in the presence of a particulate solid

(57) A spray-drying process comprises spray-drying a first material dispersed in a solvent at a concentration of 1-50% w/v in the presence of a second finely divided particulate solid material which is continuously introduced into the spray dryer in an amount from 10-99% w/w of the final product. The product is a matrix of the first material bonded to the particles of the second. The first material may comprise a gum, protein or sugar e.g. sucrose, maltodextrin, lactose, molasses and it may also comprise colourings/flavourings. The inlet temperature of the air may be 140-220°C. The second material may comprise crystalline particles e.g. sugar and /or it may be the same as the first material. The mean particle size of the second material may be 1-450 µm. A free-flowing particulate material is obtainable by such a process which may comprise an amorphous matrix of first material bonded to the second and also spheroidal particles of the first. The free-flowing material may be directly compressible and non-hygroscopic and it may be made into a tablet by compression.

GB 2 364 714 A

FIG. 1

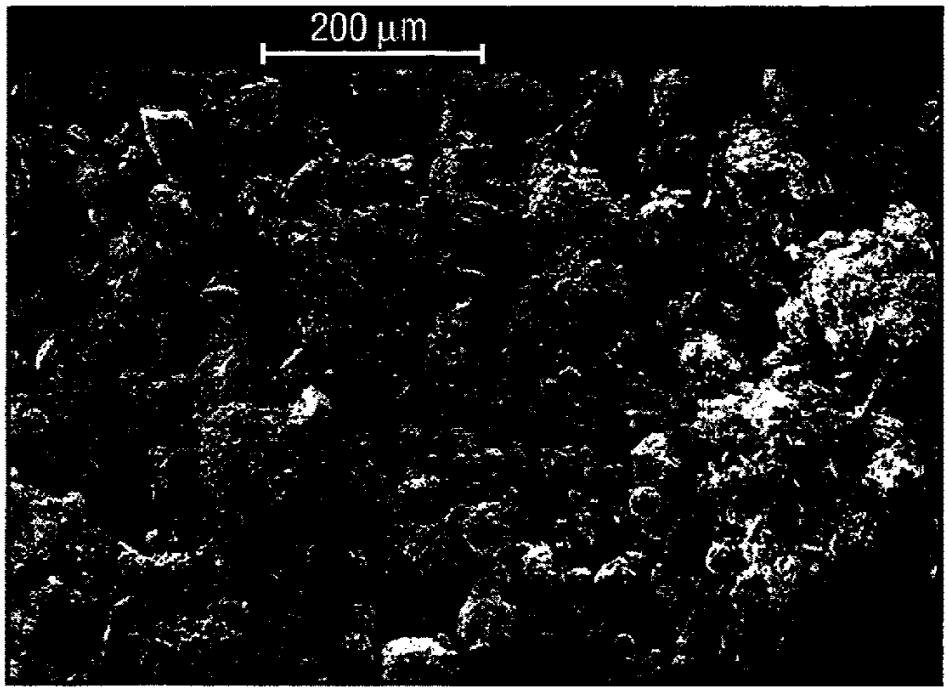


FIG. 2

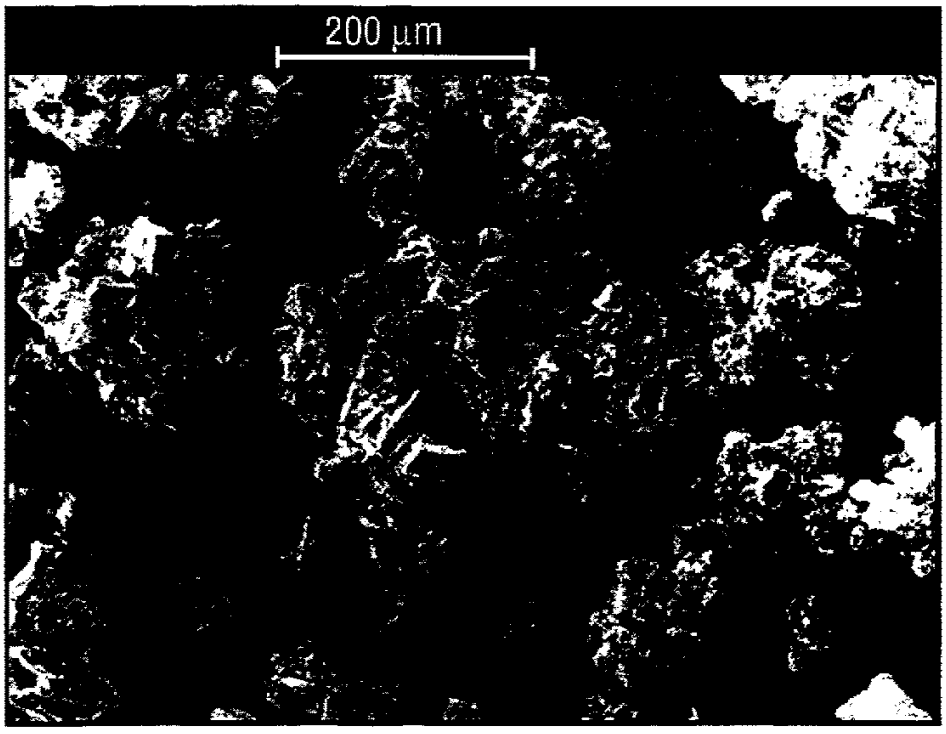


FIG. 3

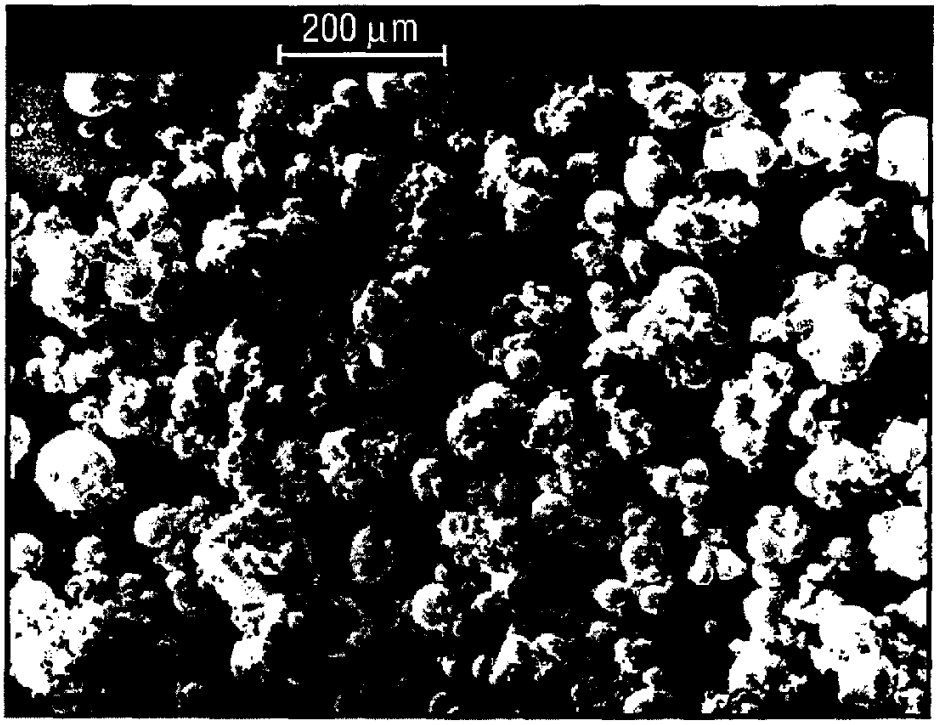
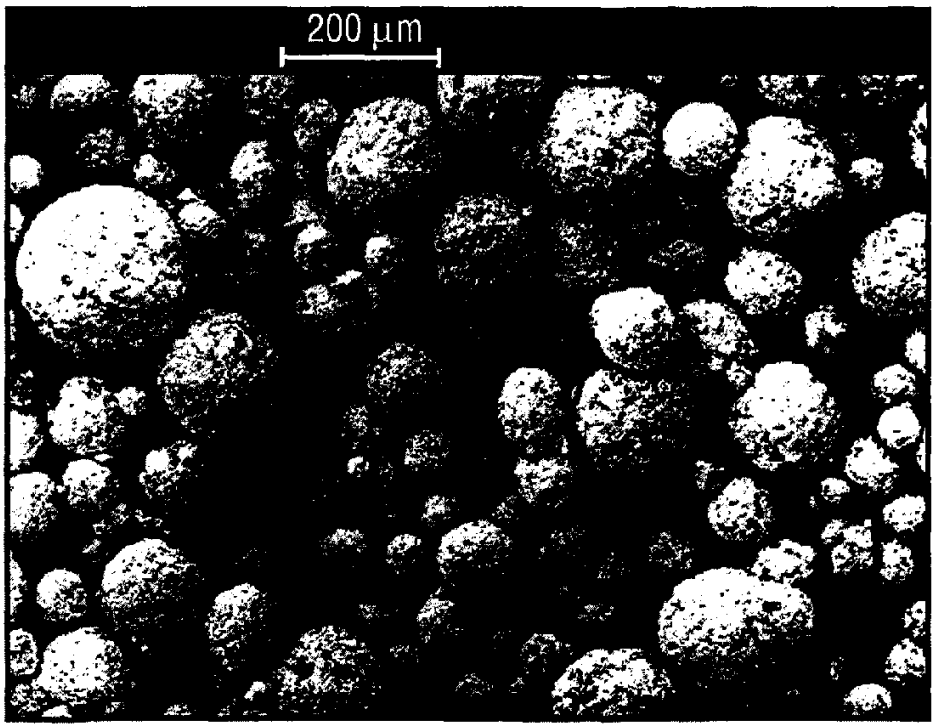


FIG. 4



METHOD OF SPRAY DRYING

This invention relates to a spray drying process which is particularly suitable for the spray drying of foodstuffs such as sugars. The invention also relates to the products of this spray drying process.

Spray drying processes are well known in the art. Generally, an aqueous dispersion of the material which is to be dried is sprayed into a hot, dry stream of gas passing through a drying chamber and the dried solids are collected. The spray drying process is used in the food industry for drying products such as milk, cream, instant coffee, cocoa, fruit and vegetable juices, extracts and flavourings. Other products such as drugs, detergents, soaps and cosmetics have also been dried in this manner.

Spray drying has also been used for the production of directly compressible forms of sugars such as lactose, sorbitol, dextrose and maltose. A directly compressible form of a material is useful since this physical form allows the material to be formed into tablets, without the use of binders or an intermediate granulation step. Certain sugars produced by a spray drying process are directly compressible. However, other sugars produced by conventional spray drying, such as sucrose, are not directly compressible. The requisite properties for a material to be directly compressible are not well understood.

One method of spray drying maltose is described in US patent 4,595,418. A process for producing powdery crystalline maltose by spray drying is described. The process is characterised by the preparation of the maltose solution to be spray dried and the low hygroscopicity of the product produced by this process.

However, it is difficult to use conventional spray drying techniques with certain materials, such as sucrose. When a sucrose solution is spray dried using conventional techniques, it rapidly forms an amorphous glass with water incorporated. The glassy sucrose will become stuck to the sides of the spray drying tower and any product collected will be sticky and hygroscopic. The hygroscopic sucrose products will be unsuitable for use in most commercial applications and are not directly compressible materials. Some other sugars, and also other materials including proteins and gums, may also form hygroscopic glasses

in a similar way when spray dried. These hygroscopic glasses are not directly compressible.

Various attempts have been made to address the problems associated with spray drying sucrose. For example, GB-A-1240691 describes a spray drying process for a solution of sucrose, wherein a proportion of solid spray-dried sucrose is recycled and introduced into the spray drying chamber as seed particles. These seed particles act to produce a microcrystalline spray dried product. The sucrose solution has a solid content of at least 70% by weight and is typically saturated, or even super-saturated. However, the product of this process may be compressed into moulds and tablets only when it is still soft and hot.

GB-A-1386379 describes a method of spray drying a sucrose solution, wherein recycled solid product is introduced into the spray drying chamber. The spray drying chamber has a heated inlet at a temperature of at least 204°C, typically 218°C to 246°C, and the sucrose-containing solution has a solids content of from 60 to 90% by weight. It is alleged that this method substantially reduces the drying time in the spray drier.

US patent 3,615,723 describes a spray drying process wherein a screen is positioned to receive the spray. The spray forms a mat on the screen and hot air is drawn through the mat for the purposes of drying the material deposited on the screen. Some of the dried material may be recycled and introduced into the spray drying chamber in solid form. It is alleged that this process improves drying efficiency.

These processes are difficult to carry out in practice. Moreover, none of the processes is capable of producing spray dried sucrose which is directly compressible. Other technologies are used commercially to produce directly compressible sucrose, such as co-crystallisation (Domino DI-PAC (Registered Trade Mark), Tate & Lyle MICROTAL (Registered Trade Mark)), fluid bed agglomeration (Sudzucker COMPRISUGAR (Registered Trade Mark)) or wet granulation. Currently, there are no directly compressible sucrose products which are produced using spray drying technology.

It is an object of the present invention to provide a widely applicable spray drying process which is capable of producing stable food products which are free flowing, non-

hygroscopic and directly compressible. It is a further object of this invention to provide a spray drying process which is capable of producing brown sugars with these same properties and which have a high molasses content. It is yet a further object of the present invention to provide a process which is capable of producing tabletted, coloured sugar products which do not suffer from undesirable mottling.

Accordingly, the present invention provides a spray-drying process comprising: providing a dispersion of a first material in a liquid solvent at a concentration of from 1 to 50% w/v; providing finely divided solid particles of a second material; spray drying the solution while continuously introducing the finely divided solid particles into the spray drier in an amount of from 10 to 99% by weight, based on the weight of the final product; whereby the process produces composite particles consisting of a spray-dried matrix of the first material bonded to particles of the second material.

Preferably, the first material comprises a sugar, a gum or a protein. More preferably, the first material comprises a sugar or sugar-based substance. Examples of suitable sugars or sugar-based substances include molasses, honey, invert, maltodextrin, glucose syrup, sucrose, glucose, fructose, lactose, sorbitol, dextrose, maltose, polyols and mixtures thereof. More preferably, the first material consists essentially of sucrose, invert, maltodextrin, lactose, molasses or mixtures thereof. Preferably, the solvent in which the first material is dispersed is water.

In one aspect of the present invention, there is provided a dispersion of the first material together with colourings and/or flavourings. Examples of suitable colourings and flavourings are Eurolake Sunset Yellow, Orange Flavour, Eurolake Blue and mint oil. The colourings and/or flavourings may be added to the solution of the first material in the presence of surfactants and/or emollients to improve their solubility.

Preferably, the second material comprises finely divided particles of a sugar. More preferably, the second material comprises sucrose, trehalose, fructose, maltodextrin, glucose syrup solids, or mixtures thereof. In one aspect of the present invention, the second material has been prepared by a spray drying process. In this aspect of the present invention, the second material may be recycled spray dried material.

Preferably, the second material consists essentially of finely divided crystalline particles.

Preferably, the mean particle size of the second material is from 1 to 450 μm. More preferably, the particle size is from 1 to 50 μm. Some preferred materials are sucrose in the form of ordinary icing sugar (mean particle size of about 25 μm) or finer icing sugar (mean particle size of about 10 μm), such as SILK (Registered Trade Mark of British Sugar PLC). Other suitable sugars include caster sugar (mean particle size of about 300 μm). The mean particle size may be determined by any suitable technique such as Laser scattering.

Preferably, the amount of second material is added in an amount ranging from 25% to 99%, more preferably 40% to 99%, more preferably 50% to 99%, and more preferably 70% to 99% by weight, based on the weight of the final product. Most preferably, the amount of second material is added in an amount ranging from above 80% to 99% by weight, based on the weight of the final product.

Preferably, the dispersion of the first material has a concentration in the range of 5% to 50% w/v. More preferably, the concentration of the dispersion of the first material is in the range of 5% to 20% w/v. These low concentrations of the dispersion gives the product desirable physical and chemical properties e.g. free flowing, low bulk density, improved colour intensity and improved dispersion.

Preferably, the inlet temperature of the air in the spray drier is in the range of 140 to 220°C. More preferably, the inlet temperature is in the range of 160 to 200°C.

In one aspect of the present invention, there is provided a spray-drying process, wherein: the first material is sucrose dissolved in water at a concentration of 5 to 50% w/v; the inlet temperature of the sucrose dissolved in water is about 190°C; the second material is a powdered crystalline sucrose having a mean size of 5 to 50μm, and the second material is added in an amount of from 80% to 90% based on the weight of the final product. In an alternative embodiment of this aspect of the present invention, the first material is sucrose dissolved in water which additionally comprises a colouring and/or flavouring dissolved in the same solution of water.

In another aspect of the present invention, there is provided a spray drying process wherein: the first material is molasses dissolved in water at a concentration of 5 to 50% w/v; the inlet temperature of the air is about 190°C; the second material is a powdered crystalline sucrose having a mean particle size of 5 to 50 μm; and the second material is added in an amount of from 80% to 95% by weight based on the weight of the final product.

The present invention also provides a free flowing particulate material obtainable by a process according to the present invention, wherein at least a fraction of the particles comprise a spray dried matrix of a first material bonded to particles of a second material.

The present invention also provides a particulate material comprising composite particles of a substantially amorphous matrix of a first material bonded to one or more particles of a second material, and further comprising spheroidal particles of the first material.

Preferably, the particles of the second material which are bonded to the first material are crystalline.

Preferably, the particulate materials according to the present invention are directly compressible and have low hygroscopicity. By directly compressible, it is meant that the particulate material compresses very readily with the minimum of force to produce a strong, robust compact. More preferably, the particulate materials are substantially non-hygroscopic.

In one aspect of the present invention, the particulate material consists essentially of sucrose.

In another aspect of the present invention, the particulate material is brown sugar. The brown sugar may have a molasses content of up to 20% w/w on a dry weight basis. Preferably, the molasses content is in the range of 5% to 15% w/w on a dry weight basis.
In a further aspect of the present invention, the particulate material is a coloured and/or flavoured sugar, gum or protein product. Preferably, the coloured and/or flavoured food

product consists essentially of a sugar. Preferably, the coloured and/or flavoured sugar, gum or protein product may be tabletted without significant amounts of mottling.

The present invention further provides a method of tabletting comprising direct compression of a particulate material according to the present invention. The present invention further provides tabletted products obtainable from this method of tabletting.

Specific embodiments of the present invention are now described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows a Scanning Electron Micrograph (SEM) of a product produced by the process of the present invention comprising spray dried invert (5% - dry solids) and icing sugar (95%).

Figure 2 shows a SEM of icing sugar particles produced by a conventional fluid bed agglomeration process.

Figure 3 shows a SEM of particles of trehalose produced by conventional spray drying.

Figure 4 shows a SEM of particles of maltose produced by a spray drying process described in US 4,595,418.

The process of the present invention is performed using the general procedure described below on a conventional spray drier having at least two inlet ports.

A vibratory feeder is placed at a first inlet port and the dry material flow rate calculated. When the first port is opened, the material is pulled by negative pressure into the spray drying chamber. This is performed as a solution of a second material is fed into a second inlet port and is spray dried. The spray dried product is taken and collected at the base of an adjoining cyclone.

A summary of the results obtained in Examples 1-20, together with all experimental parameters is shown in Table 1.

Table 1

Example	Details	Dry Feed Ingredient (2)	Wet Feed Ingredient (1)	Concn. of (1), %	Final Product (2) %	Final Product (1) %	Inlet Temperature, °C	Outlet Temperature, °C	% Moisture Content Karl Fischer
	100% Sucrose								
1		NCP	Sucrose	8	90	10	170	70	0.49
2		NCP	Sucrose	8	90	10	190	90	0.3
3		NCP	Sucrose	8	80	20	190	90	1.24
4		Caster	Sucrose	8	90	10	190	90	0.16
5		Granulated	Sucrose	8	90	10	190	75	0.38
	Experimental design								
6		NCP	Invert	8	80	20	190	70	0.6
7		NCP	Invert	8	90	10	190	70	0.42
8		NCP	Mixture	8	89.5	10.5	190	90	0.53
9		NCP	Mixture	40	89.5	10.5	190	85	0.25
10		NCP	Maltodextrin	8	94	6	190	85	0.62
11		NCP	Lactose	8	95	5	190	80	0.42
	Browns								
12		Caster	Molasses	8	92	8	190	90	0.22
13		Caster	Molasses	8	88	12	191	88	0.27
14		Granulated	Molasses	8	88	12	190	80	0.21
15		Granulated	Molasses	40	88	12	190	75	0.23
	Coloured and Flavoured								
16	50ppm Eurolake Sunset yellow	NCP	Sucrose	8	90	10	190	80	0.31
17	as16(i) + 0.2% orange flavour	NCP	Sucrose	8	90	10	190	80	0.23
18	as 16(i) + yellow and red food colours	NCP	Sucrose	8	90	10	190	80	0.23
19	300pm Eurolake blue	NCP	Sucrose	8	90	10	190	75	not measured
20	as 17(i) + 0.36 mint oil	NCP	Sucrose	8	90	10	190	75	not measured

NCP = 100% sucrose icing sugar (No Calcium Phosphate)

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Examples 1-5 (100% Sucrose Products)

Example 1

An 8% sucrose solution ("wet feed ingredient") was spray dried as NCP icing sugar ("dry feed ingredient") was continuously introduced into the spray tower. (NCP icing sugar is a 100% sucrose product with a mean particle size of 20-25 μm, containing no calcium phosphate anticaking agent). The inlet temperature of air was about 170°C. The process was left to run for approximately 1 hour. When the spray drying chamber was inspected, there was no sucrose stuck to the exterior walls as is usually associated with sucrose spray drying. The material collected was more free flowing than icing sugar. The final product consisted of 90% dry feed ingredient and 10% wet feed ingredient, based on the amounts of dry solids in the starting material.

Example 2

Example 1 was repeated using conventional spray drying temperatures. The inlet temperature was about 190°C. Similar results were obtained as those from Example 1.

Example 3

Example 2 was repeated with the difference that the dry feed ingredient and wet feed ingredient were introduced into the spray drying tower such that the final product consisted of 80% dry feed ingredient and 20% wet feed ingredient, based on of the amounts of dry solids in the starting material.

Example 4

Example 2 was repeated with the difference that the dry feed ingredient was caster sugar. The product obtained displayed very different flow characteristics to caster sugar and was found to be more compressible than caster sugar.

Example 5

Example 2 was repeated with the difference that the dry feed ingredient was granulated sugar.

Examples 6-11

These Examples were performed in accordance with the process parameters shown in Table 1.

Example 6 produced excellent visible agglomerates and excellent flow characteristics. Some sticking on the exterior walls of the spray drier was observed.

Example 7 produced a good flowable powder with smaller agglomerates than Example 6. No processing problems were observed.

In Examples 8 and 9, "mixture" refers to a mixture of sucrose, invert, maltodextrin, and lactose. Example 9 used a 40% w/v wet feed solution. The product was finer than those Examples using an 8% w/v wet feed solution and had poorer flow characteristics.

Examples 12-15 (Brown Sugar Products)

These Examples were performed in accordance with the process parameters shown in Table 1.

Molasses was added to both caster and granulated sugars in order to determine how uniformly and effectively the spray dried material sticks to the sugar crystals.

Examples 12 and 13 both successfully produced a spray dried brown sugar product at 8% and 12% molasses on dry product. The product was more flowable than normal brown sugar. This is due to the lower moisture content and possibly the spray dried material rounding the edges of the caster crystals. Both samples were tacky when collected and needed to be broken up until dry to maintain their flow.

Examples 14 and 15 employed granulated sugar. Some separation of the spray dried material from the sugar crystals was observed.

Examples 16-20 (Coloured and Flavoured Products)

These Examples were performed in accordance with the process parameters shown in Table 1. All of Examples 16-20 tabletted successfully to produce tablets with little mottling.

Examples 16-18 produced products with solely orange colour and also with orange flavour. Both the colours and flavours were added to the solution of sucrose to be spray dried (wet feed ingredient).

In Example 17, addition of orange flavour produced an orange dextrose type flavour.

In Example 18, the colour of the yellow flavour was intensified by the addition of food colours.

Examples 19 and 20 produced strong deep blue coloured powders. In Example 20, mint oil was added to the sucrose solution, in addition to the blue colouring. Emulsifiers and/or surfactants may optionally be added to the solution to improve mixing.

The above Examples demonstrate some of the advantages of the present invention over the processes known in the prior art. All of the Examples produced free flowing, substantially non-hygroscopic products which were compressible and could be tabletted successfully to produce tablets.

A particular advantage illustrated in Examples 12 to 15 is the low moisture content of the brown sugar products. This produces brown sugar products which are more flowable than those products made by conventional methods. Brown sugar is currently produced by adding a volume of molasses onto a mixer containing the appropriate weight of sugar of suitable particle size (e.g. caster, granulated or medium sugar).

A further advantage illustrated in Examples 13 to 15 is that the process of the present invention enables the production of high molasses content sugars. Such sugars have a market in, for example, Christmas cake manufacture. Examples of typical brown sugar products are soft light brown (caster, 0.5% moisture, 2% molasses), soft dark brown (caster, 2.5% moisture, 8% molasses), and demerara sugar (medium sugar, 0.5% moisture, 1% molasses). Using conventional methods, the level of 8% molasses on the soft dark brown cannot be increased due to the viscosity of the molasses used. Any higher addition rates and the molasses will not stick to the sugar crystal. However, brown sugars produced according to Examples 13 to 15 of the present invention have a molasses content of 12%. In particular, Example 13, having 88% caster and 12% molasses, showed good flowability with no separation of the molasses from the caster being observed.

A particular advantage illustrated in Examples 16 to 20 is that little or no mottling was observed when the sugar products were tabletted. Traditionally, tabletted confectionary is very difficult to colour. In conventional processes, dry powders are added to the agglomerate before tabletting which results in a mottled and pastel coloured tablet. By contrast, in the present invention (Example 16 to 20), the colour is added to the wet feed solution prior to spray drying. Thus, the colour becomes an integral part of the agglomerate, and upon tabletting a stronger coloured tablet is produced without mottling.

Furthermore, the process of the present invention is cheaper than conventional processes in some cases.

With these advantages of the present invention in mind, it is envisaged that the process of the present invention can be applied advantageously to a produce a number of food products. These food products will have improved properties compared to products made by conventional methods. In some cases (e.g. honey), novel, powdered forms of a natural liquid food product will be available.

Suitable products include brown sugar, dry and icing fondant mixes, honey, invert, glucose syrup, sucrose, fructose, maltose, lactose, polyols, chocolate crumb, sweeteners, instant

gums, instant proteins, beverage/dessert mixes. Such products will be available in a stable, free flowing, substantially non-hygroscopic, compressible, and optionally coloured form.

Without wishing to be bound by theory, it is believed that the inventive process produces novel products with the above-mentioned advantages by the way in which the solid ingredient in the spray drier coats the particles of spray dried material while they are still wet.

Scanning electron microscopy (SEM) shows that the final spray dried product consists mainly of crystalline particles of the solid ingredient bonded to the particles of spray dried ingredient in glassy form. Thus, the product differs fundamentally from the materials produced by seeding in the prior art (e.g. GB 1,240,691) which are essentially crystalline. The structure of the spray dried products typically produced by the present invention can be seen in Figure 1. There is a combination of mostly coral-like composite particles together with a few glassy spheroidal particles. It is believed that this unique structure gives the material its inherent direct compressibility.

By contrast, Figure 2 shows crystalline coral-like structures produced by a conventional fluid bed agglomeration process. No glassy spheroidal particles are present in this structure.

In Figure 3, there are the usual agglomerated glassy spheroidal particles produced by a conventional spray drying process.

In Figure 4, it can be seen that an alternative spray drying process, as described in US 4,595,418, produces a structure with glassy spheroidal particles coated with microcrystalline material.

Thus, it has been demonstrated that the process of the present invention produces a particulate material which has a unique structure, as compared to other spray drying or fluid bed agglomeration processes.

It will, of course, be understood that the present invention has been described by way of example, and that modifications of detail can be made within the scope of the invention.

Claims:

1. A spray-drying process comprising: providing a dispersion of a first material in a liquid solvent at a concentration of from 1 to 50% w/v; providing finely divided solid particles of a second material; spray drying the dispersion while continuously introducing the finely divided solid particles into the spray drier in an amount of from 10 to 99% by weight, based on the weight of the final product; whereby the process produces composite particles consisting of a spray-dried matrix of the first material bonded to particles of the second material.

2. A spray-drying process according to claim 1, wherein the first material comprises a sugar, a gum or a protein.

3. A spray-drying process according to claim 2, wherein the first material comprises a major fraction of a sugar.

4. A spray-drying process according to claim 3, wherein the first material consists essentially of sucrose, invert, maltodextrin, lactose, molasses or mixtures thereof.

5. A spray-drying process according to any preceding claim, wherein the dispersion of the first material additionally comprises colourings and/or flavourings.

6. A spray-drying process according to any preceding claim, wherein the dispersion of the first material has a concentration in the range of 5% to 50% w/v.

7. A spray-drying process according to any preceding claim, wherein the inlet temperature of the air as it enters the spray drier is in the range of 140°C to 220°C.

8. A spray-drying process according to any preceding claim, wherein the second material consists essentially of finely divided crystalline particles.

9. A spray-drying process according to any preceding claim, wherein the second material comprises a sugar.

10. A spray-drying process according to claim 9, wherein the second material consists essentially of finely divided crystalline sugar.

11. A spray-drying process according to any preceding claim, wherein the mean particle size of the second material is from 1 to 450μm.

12. A spray-drying process according to claim 11, wherein the mean particle size of the second material is from 5 to 50μm.

13. A spray-drying process according to any preceding claim, wherein the first and second materials are the same.

14. A spray-drying process according to any preceding claim, wherein the second material is added in an amount of from 50% to 99% by weight, based on the weight of the final product.

15. A spray-drying process according to any preceding claim, wherein: the first material is sucrose dissolved in water at a concentration of 5 to 50% w/v; the inlet temperature of the air is about 190°C; the second material is a powdered crystalline sucrose having a mean size of 5 to 50μm, and the second material is added in an amount of 80% to 90% based on the weight of the final product.

16. A spray-drying process according to claim 15 wherein the first material is sucrose dissolved in water which additionally comprises a colouring and/or flavouring dissolved in the same solution of water.

17. A spray-drying process according to any one of claims 1 to 14, wherein: the first material is molasses dissolved in water at a concentration of 5 to 50% w/v; the inlet temperature of the air is about 190°C; the second material is a powdered crystalline sucrose having a mean size of 5 to 50μm, and the second material is added in an amount of 80% to 90% based on the weight of the final product.

18. A free flowing particulate material obtainable by a process according to any preceding claim, wherein at least a fraction of the particles comprise a spray-dried matrix of a first material bonded to particles of a second material.

19. A free flowing particulate material comprising composite particles of a substantially amorphous matrix of a first material bonded to one or more particles of a second material, and further comprising spheroidal particles of the first material.

20. A particulate material according to claim 18 or 19, which is directly compressible.

21. A particulate material according to claim 18, 19 or 20, which is substantially non-hygroscopic.

22. A particulate material according to any one of claims 18 to 21 wherein the particles of the second material which are bonded to the first material are crystalline.

23. A particulate material according to any one of claims 18 to 22 consisting essentially of sucrose.

24. A particulate material according to any one of claims 18 to 22 which is brown sugar.

25. A particulate material according to any one of claims 18 to 22 which is a coloured and/or flavoured sugar, gum or protein.

26. A method of tabletting a particulate material according to any one of claims 18 to 25 comprising a direct compression step.

27. A tablet obtainable by the method of claim 26.

Application No:	GB 0017525.7	**Examiner:**	Dr Fatema Sardharwala
Claims searched:	1-27	**Date of search:**	19 January 2001

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C6B (B8), B1B (BKA2)

Int Cl (Ed.7): A23L 3/46; B01D 1/18; C13F 1/02

Other: Online: EPODOC, WPI, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0749770 A1	(STORK) whole document, esp. line 54 of column 6 to line 51 of column 7	18, 19
X	US 4162926	(VELTMAN et al.) whole document, esp. Examples	18, 19
X	US 3956009	(LUNDQUIST et al.) whole document, esp. line 66 of column 1 to line 18 of column 2; lines 57-66 of column 2 and Examples	1-4, 6-11, 13, 14, 18, 19 22, 23

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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(54) Title Process and spray drying apparatus for stable particle agglomerates

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(73) Patent Granted to NIRO HOLDING A/S, A COMPANY ORGANISED UNDER THE LAWS OF DENMARK, OF NO. 6, BREDGADE, DK-1260 COPENHAGEN K, DENMARK.

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Process and spray drying apparatus for producing stable particle agglomerates.

The present invention deals with a process for spray drying liquids containing dissolved or suspended solids to produce stable particle agglomerates, as well as a spray drying apparatus for use in the process.

Powdery materials produced by spray drying of solutions or suspensions, such as milk powders, are very often required to have so-called instant properties. The term "instant" means readily dispersible or readily soluble in liquids, especially aqueous liquids.

To obtain instant properties of a spray dried powder it is usually essential that it consists of agglomerates of primary particles. For products containing only a minor portion of fat, such as skim milk powders, agglomeration is the only process which is necessary to achieve instant properties in cold water, whereas fat-containing products require an additional treatment, viz. a coating with a component having both lipophilic and hydrophilic properties to cover the water repellant fatty layer normally present on the surface of the particles or agglomerates.

Non-agglomerated spray dried powders consist of single particles which, when milk powders are concerned, usually have a mean size in the range 40-100 microns. Such powders are relatively heavy, inter alia they have high bulk density, are dusty and difficult to reconstitute in water. When such powder is poured into water a heap of powder forms on the water surface, and at the first contact of the water with the heap of powder a particle slurry is formed at the interface which avoids penetration of water to the interior of the heap of powder. Consequently, only a minor part of

the powder is dispersed or dissolved resulting in a weak solution or suspension containing lumps wetted only on the surface and containing dry powder inside.

An agglomeration process transforms the single particles into clusters of particles called agglomerates. Agglomerating increases the mean particle size and decreases the bulk density (the term "mean particle size" here denotes mean size of the elements of the powder which can be either single particles or agglomerates). Therefore, agglomerated powders are considerably more voluminous than conventional powders. This is because they have higher content of interstitial air which means the air inside and between the agglomerates. At the reconstitution this high content of interstitial air is replaced by water allowing the agglomerates to disperse and disintegrate to form a solution or suspension without lumps.

Thus, a controlled agglomeration (possibly combined with the above mentioned treatment with lipophilic and hydrophilic agents) is by far the most essential measure to obtain a suitable wettability and dispersibility and other properties of spray dried powders to ensure the desired instant characteristics thereof.

A description of methods hitherto used for agglomerating spray dried powder is presented in the following paper: J. Due Jensen: "Agglomerating, Instantizing and Spray Drying" Food Technology 60-71 (1975).

The various methods available for agglomeration of spray dried powders may be termed either rewet processes or straight-through processes. Rewet processes are carried out after the powder has been manufactured whereas in the straight-through processes agglomeration takes place during the spray drying, i.e. during and immediately after the primary particles have been formed.

In a typical straight-through process, fine particles, i.e. non-agglomerated particles, produced in the spray drying step, are recycled to meet liquid droplets or moist sticky particles in the atomization zone.

When an atomizer wheel is used for atomizing the liquid to be spray dried, the fine particles are being recycled to a fixed location just above the periphery through an annular opening of the atomiser housing of said wheel as illustrated in the above mentioned paper or they may be blown upwards against the atomized droplets from a position centrally below the atomizer wheel as also illustrated in said paper.

It has also been suggested (DE-A 1 228 567, Max E. Schultz) to blow the fine particles by means of moisturing steam and optionally pressurized air in a direction radial to the atomizer wheel to force the fine particles into the cloud of atomized droplets and partly dried particles counter-currently thereto. However, by this method a mixture is formed consisting of agglomerates of very different structure and size.

Therefore prior art processes are not so efficient as desirable as to ensure that a large proportion of the recycled fine particles are incorporated into agglomerates of the desired structure, size and mechanical strength.

It has now turned out that adjustment of the location for recycling of the fine particles in relation to the atomizer wheel and other parameters as defined below enables obtainment of a larger proportion of agglomerates of desired structure, particle size and strength.

This fact is utilized in the process according to the present invention which deals with a process for spray drying liquids containing dissolved or suspended solids to produce stable particle agglomerates, wherein the liquid is atomized in a drying chamber by means of

an atomizer wheel to form droplets; a stream of drying air encircling the atomizer wheel is conducted against the ejected droplets in directions predominantly transversely to the paths of these, whereby the droplets are dried to form a particulate material; and the finest fraction of particles of said material is recovered and recycled pneumatically to the drying chamber to collide with ejected droplets or only partly dried more or less sticky particles, which process according to the invention is characterized in

(i) introducing said finest particles into the stream of drying air before it meets the ejected partly dried droplets, and dispersing said particles in a minor portion only of the stream of drying air, whereby said finest particles will be entrained in the drying air to collide with the partly dried droplets at a defined distance from the wheel perphery, and

(ii) adjusting the location for the introduction of said finest particles to adjust said defined distance of the place for collision from the wheel in dependency of the characteristics of the liquid to be dried and operational parameters, to obtain agglomerates of desired structure and particle size distribution.

The above mentioned adjusting of the location for the introduction of the finest particles to be recycled may be performed without undue experimentation by a skilled person who considers the explanation below as to the relationship between the distance of the area, where the finest particles are contacted with the droplets or only partly dried sticky particles from the wheel periphery, and the structure of the resulting agglomerates.

1) If the location for the introduction of the finest particles is adjusted to have only a very short distance from the atomizer wheel periphery to the area where the finest particles meet the atomized droplets, only a minor evaporation has taken place from the droplets and they are still predominantly liquid. The fine particles which meet these liquid droplets either penetrate into the interior of these or the surface of the fine particles are coated with the droplets. In this last mentioned case the so called "onion"-structure is formed. Both these cases result in a single particle of increased size and often exhibiting some deformation. The two type of structures are shown on fig. 1 as structure a and b, resp. Both structures have high mechanical stability and low specific bulk volume and are not agglomerates desired in instant powders.

2) If the distance of the area where the collision takes place from the wheel is somewhat longer, evaporation from the droplets has proceeded further but the moisture content will still be sufficient to retain plasticity and the fine particles penetrate partly into the droplet surface producing a pseudo-agglomerate which may be described as "raspberry"-structure (c on fig. 1). Obviously, such structure has not much porosity and consequently the specific bulk volume is rather low. Thus structure c is not ideal, either when an instant product is desired.

3) When the distance from the wheel to the above defined collision area is even longer, the atomized droplets have been transformed into solid particles of little plasticity which are still sufficient sticky and true agglomerates with high porosity and "grape"-structure result (structure d in fig. 1). The result-

ing powder has high specific bulk volume. The mechanical stability is less than that of the particles of structure a, b or c but sufficient to enable mechanical handling for instance in canning apparatuses.

4) When the collision area is at even longer distance from the wheel the particles created by the drying of the atomized droplets have low moisture content and therefore low stickiness, and the agglomerates created are of "loose grape-structure". (Structure e on fig 1).

When milk powder is dealt with the most desired structure will be a structure of the compact grape type (d).

Thus, it is possible without undue experimentation to adjust the above defined distance to obtain the desired agglomerate structure and to compensate for variations of operational features which would otherwise influence the quality of the product. Examples of such operational features are concentration and temperature of the feed, pre-heat treatment of the feed (when the feed is a milk product), drying air flow, rotational speed of the atomizer wheel, etc.

The invention also comprises a spray drying apparatus for performing the process, comprising a drying chamber having an atomizer wheel therein for injecting droplets of the liquid to be spray dried into the drying chamber, means for providing a stream of drying air around the atomizer wheel and predominantly transversely to the path in which the droplets are ejected from the wheel, a particle separator for recovering the finest spray dried particles from the drying air, and means for recycling these finest particles to the drying chamber, which spray drying appararus according to the invention is characterized in that said means for recycling the finest particles comprise at least one

conduit debouching in the drying chamber at a location which, when the apparatus is in operation, is within the stream of drying air and upstream of the area where said drying air meets the ejected droplets, and the location for the debouching of said at least one conduit is adjustable to enable a variation of the distance between said area where the recycled fine particles entrained in drying air meet the ejected droplets, and the atomizer wheel periphery.

Several mechanical constructions may be utilized to obtain the necessary possibility for adjusting the above defined distance crucial to the characteristics of the resulting agglomerates.

In one of the preferred embodiments of the spray drying apparatus according to the invention the atomizer wheel is mounted on an atomizer housing of conical shape having its smallest diameter adjacent to the wheel and around this housing is a drying air disperser providing a stream of drying air close to the outer wall of said conical housing and in directions parallel thereto, which apparatus according to the invention is characterized in having a pipe for pneumatic introduction of fine particles to be recycled, which pipe passes through said outer wall of the conical housing and which pipe has an aperture into the drying chamber, the rectangular distance of which aperture to the conical outer wall of the housing is adjustable.

A way to enable adjustment of said rectangular distance from said aperture to the conical wall is by telescopic variation of the lengths of that part of said pipe which projects into the drying chamber.

In connection with this last mentioned embodiment it is an advantage to have said aperture placed in the side wall near the terminal end of said pipe and that said pipe has an end portion which due to the telescopic construction may be turned to provide

further possibility for amending the rectangular distance between the aperture and the conical housing wall.

In an alternative embodiment of the apparatus according to the invention the desired possibility for adjusting the distance between the wheel and the area where the recycled fine particles meet the ejected droplets and partly dried particles, is obtained by having the location for the debouching of said, at least one conduit adjustable by means of a swivel joint in that part of the conduit which extends into the drying chamber.

This last mentioned embodiment is suitable not only in connection with spray drying apparatuses having a conical atomizer housing but also where said housing has other shapes, for example being cylindrical.

The same applies to a further, and preferred, embodiment in which the pipe for introducing the particles to be recycled at the terminal end thereof is provided with a turnable slide (called deflector), able to divert said particles in a direction at an angle with the centerline of said pipe, which deflector may be turned to pneumatically inject said particles in any direction substantially rectangular to the pipe.

Needless to say that further variations of bulk volume can be achieved when turning the deflectors of a multi-discharge pipe unit in various directions.

By utilizing the present invention to obtain optimal conditions for creation of desired agglomerates, the amount of fine particles which have to be recycled is reduced. Such a reduction is advantageous since any recycling to the heat and moist conditions in the spray drying chamber involves a risk of heat damage resulting in reduced product qualities, for instance reduced solubility.

Thus, the advantage of the present invention is

not restricted to the obtainment of agglomerates of desired structure, also other product qualities are improved, especially when heat sensitive materials are produced.

The invention is further elucidated with reference to the drawing, where

Fig. 1 schematically illustrates the influence of the distance between the atomizer wheel and the area where the fine particles are contacted with the droplets or partly dried particles on product structure, specific bulk volume and mechanical stability, as previously referred to,

Fig. 2 schematically shows an embodiment of a plant for the manufacture of spray dried instant whole milk or other fat containing food powder by the process according to the invention, which plant comprises a spray drying apparatus according to the invention,

Fig. 3 schematically depicts an embodiment of a detail of the apparatus shown in fig. 2 within the rectangle I,

Fig. 4 schematically shows an other embodiment of the detail within the rectangle I in fig. 2,

Fig. 5 schematically depicts a further embodiment of the detail within the rectangle I in fig. 2,

Fig. 6 is a graph belonging to the Examples 1-12 below,

Fig. 7 is an electron micrograph showing agglomerates obtained i Example 3 below, and

Fig. 8 is an electron micrograph showing agglomerates obtained in Example 10 below.

In fig. 2 a stream of hot drying air is supplied

via a duct 1 to a drying air disperser 2 at the ceiling of a spray drying chamber 3.

Concentrated whole milk is via conduit 4 fed to an atomizer wheel 5 from which it is ejected as droplets. By contact with the downward stream of hot drying air provided by the air disperser 2 said droplets are transformed into milk powder. A substantial part of said milk powder leaves the bottom of the drying chamber while still having a higher moisture content than the one desired in the final product.

This powder falls into a vibrated fluidized bed drying apparatus 6 from where it with a reduced moisture content is let to a further vibrated fluidized bed drving apparatus 7 from where it passes on to a lecithin treatment unit 8 to be sprayed with lecithin dissolved in edible oil or fat.

After this lecithin treatment the powder is passed through a further vibrated fluidized bed apparatus 9 to further condition the powder as conventional.

The drying air leaves the spray drying chamber 3 through a duct 10. A substantial amount of fine powder particles are entrained by the drying air passing through duct 10 which are separated from the air in a cyclone 11. The drying air leaves the cyclone through a stack 12.

The three vibrated fluidized bed apparatuses 6, 7 and 9 receive conditioning air, as indicated by 13, 14 and 15, which passes through the fluidized powder layer maintained in each fluidized bed apparatus. Thereby a substantial part of the finest particles in the fluidized layers are blown off and removed from the fluidized layers by the air which leaves the vibrated fluidized bed apparatuses through the conduits 16, 17 and 18, resp.

The outlet air with entrained fine particles

from the three fluidized bed apparatuses is led into a cyclone 19 to recover the fine particles.

The fine particles recovered in the cyclones 11 and 19 are pneumatically recycled to the spray drying chamber 3 via pipe 20.

The essential features of the present invention relates to the debouchment of pipe 20 into the spray drying chamber. Said debouchment is depicted on fig. 3 4 and 5.

On fig. 3, the numbers 5 and 20 have the same significance as on fig. 2. 21 represents the outer wall of a conical housing surrounding the atomizer, through which wall the end of the pipe 20 passes into the drying chamber.

In the embodiment depicted in fig. 3 the end of the pipe 20 is provided with a telescopic extension 22, the position of which in the pipe 20 can be adjusted not only vertically but also by turning the extension around its longitudinal axis.

At its bottom end said extension has an aperture 23 in one side whereas the opposite side and the bottom is formed as a deflecting member to enable smooth pneumatic passage of the recycled fine particles out through the aperture 23.

From the drying air disperser 2 shown in fig. 2, a stream of drying air passes downward along the wall 21 and in directions substantially parallel thereto, as indicated by the arrows in fig. 3, 4 and 5.

The direction of this stream of drying air usually also has a certain rotational component which, for the sake of simplicity, is disregarded in the present explanation.

The fine recycled particles which reach the drying chamber through the aperture 23 will disperse in a portion of the stream of drying air, and entrained in the drying air they are carried downward to collide

with droplets ejected from the wheel 5 and partly dried particles. On fig. 3, 4 and 5 the distance from the wheel periphery to the area where said collision takes place is indicated by a.

By varying the distance a it is possible to adjust the agglomeration as explained above and further illustrated in the Examples below.

As it is obvious from fig. 3 any change of the rectangular distance b from the aperture 23 to the wall 21 will be reflected in a corresponding change of the distance a.

The distance b (and consequently a) may be decreased by fixing the extension 22 in a higher position in the pipe 20, whereas an increase of the distance b may be achieved by fixing the extension 22 in a lower position and/or by turning the extension to have the aperture 23 directed away from the wheel 5 or to have it in an intermediate position.

In the embodiment of fig. 4 an extension 24 is connected to the pipe 20 by means of a swivel joint 25 whereas the remaining part of the extension corresponds to extension 22 shown on fig. 3.

In the embodiment of fig. 4 the distance a may be adjusted either by bending the extension towards or away from the atomizer wheel or by turning the aperture 23 more or less away from the atomizer wheel or by utilizing both these measures.

The embodiment of fig. 4 with swivel joint is suitable not only in connection with spray drying apparatuses having conical atomizer housing constructions but also in connection with apparatuses having cylindrical atomizer housing.

In the embodiment depicted on fig. 5 the pipe 20 is provided with a deflector 26 releasably and turnably arranged in a bushing 27. The deflector guides the fine particles out into the drying chamber

through an aperture 28 the position of which may be altered by turning the deflector. This embodiment enables an adjustment of the distance "a" within limits somewhat narrower than the limits existing for the embodiments in fig. 3 and 4 but it will satisfy the requirements of most commercial plants, and the embodiment is preferred due to simplicity and reliability.

In spray dryers with an air flow pattern of a substantially rotary nature, the effect of turnable deflectors on the distance "a" (fig. 3, 4 and 5) will be determined by a complicated balance of mass and momentum flows of the rotating drying air and the stream of fine particles and their accompanying transport air. It is obvious, however, that the distance "a" will be longer when the fine particles are injected in a co-current direction than when they are injected in a counter-current direction (with regard to the direction of the stream of drying air). The effect on the specific bulk volume of the resulting powder will differ in a similar way.

The spray drying apparatus according to the invention preferably has a plurality of adjustable means for introducing the recycled fines. For simplicity only two such means are indicated on fig. 2, but four or six or even more such means are regarded as preferred in apparatuses for commercial production.

The invention is further illustrated by means of the following Examples.

EXAMPLES 1 - 12

These Examples were performed in a plant as the one illustrated in fig. 2 utilizing recycling measures as illustrated in fig. 3. The number of recycling pipes with extensions in the spray drying apparatus was 4.

The purpose of these Examples was to demonstrate the possibility of varying the degree of agglomeration (expressed in terms of specific bulk volume) by adjusting the distance b (and thereby a) in fig. 3.

The feed to be atomized was concentrated whole milk.

All these twelve Examples were performed using identical operational parameters except that the distance b was different in each Example. The distance b was adjusted from 57 mm to 203 mm by telescopic adjustment of the extension 22 in the pipe 20 and by turning the direction of the aperture 23 more or less towards or away from the atomizer wheel.

The results appear from the following Table.

T A B L E

Example	b, mm	Specific bulk volume ml/100g	Bulk density kg/m^3
1	57	220	455
2	75	230	435
3	93	240	417
4	107	240	417
5	125	242	413
6	143	256	391
7	147	257	389
8	160	257	389
9	176	261	383
10	177	264	379
11	195	275	364
12	203	280	357

A graph based on the above values is presented in fig. 6. from which it appears that an approximately

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linear relationship exists between specific bulk volume and the distance b (and consequently also the distance a), at least within the range covered by the twelve Examples.

Samples of the products from Example 3 and 10 were subjected to electron microscopy.

Fig. 7 shows, at a magnification of 400 diameters, agglomerates obtained in Example 3. These agglomerates have the structure which above is described as "compact grape".

Fig. 8 shows at a magnification of 500 diameters material obtained in Example 10. As expected the structure here is substantially less compact than the one obtained in Example 3. The amount of interstitial air between the primary particles is higher and the areas of contact between the primary particles are smaller, and the agglomerate shown is of the type above termed "loose grape".

EXAMPLE 13

Also this Example was performed in a plant as the one illustrated in fig. 2 in which the spray drying apparatus had four fine particle recycling means constructed as shown in fig. 3.

The spray drying chamber had a diameter of 9.9 m and a cylindrical height of 9.6 m. The top angle of the conical bottom part of the chamber was 60°.

9800 kg whole milk concentrate with 48% total solids and 28% fat in solids and at a temperature of 70°C was atomized per hour.

The temperature of the main drying air provided through duct 1 to the chamber was 180°C. The outlet temperature was adjusted to give approximately 6 % moisture in the powder recovered from the bottom of the drying chamber.

The final drying of the powder took place in the three vibrated fluidized bed apparatuses 6, 7 and 9 which were supplied with air at the following temperatures: At 13 95°C, at 14 75°C and at 15 40°C.

A lecithin solution consisting of powdered lecithin in an amount of 0,2% lecithin calculated on powder, dissolved in butter oil (40% lecithin) was sprayed onto the powder in the unit 8. The fine particles entrained in the various gas streams were recovered in the cyclones 11 and 19 and recycled through the pipe 20 and the extensions 22. The rectangular distances b to the conical wall 21 (fig. 3) were 203 mm (applies to each of the four extensions).

The amount of fine powder recycled per hour through 20 corresponded to 16-21% of the product recovered from 9, which is a relative small proportion.

The instant whole milk powder obtained had the following characteristics:

	Specific bulk volume	Bulk density
Tapped 0 x:	286 ml/100 g	350 kg/m3
Tapped 100 x:	240 ml/100 g	417 kg/m^3
Tappet 1250 x:	227 ml/100 g	440 kg/m^3

Solubility index: < 0.1 (ADMI)

Wettability: 6 sec. (IDF method 87:1979)

Particle size distribution:

>500	microns	5%
355- 500	"	10%
250- 355	"	19%
212- 250	"	12%
180- 212	"	15%
150- 180	"	11%
125- 150	"	9%
90- 125	"	10%
< 90	"	9%.

Particle density 1.17 g/ccm (NA Method A11a)

Flowability: 52 sec. (NA Method A23a).

PATENT CLAIMS

1. A process for spray drying liquids containing dissolved or suspended solids to produce stable particle agglomerates, wherein the liquid is atomized in a drying chamber by means of an atomizer wheel to form droplets; a stream of drying air encircling the atomizer wheel is conducted against the ejected droplets in directions predominantly transversely to the paths of these, whereby the droplets are dried to form a particulate material; and the finest fraction of particles of said material is recovered and recycled pneumatically to the drying chamber to collide with ejected droplets or only partly dried more or less sticky particles, characterized in

(i) introducing said finest particles into the stream of drying air before it meets the ejected partly dried droplets, and dispersing said particles in a minor portion only of the stream of drying air, whereby said finest particles will be entrained in the drying air to collide with the partly dried droplets at a defined distance from the wheel, and

(ii) adjusting the location for the introduction of said finest particles to adjust said defined distance of the place for collision from the wheel in dependency of the characteristics of the liquid to be dried and operational parameters, to obtain agglomerates of desired structure.

2. A spray drying apparatus for performing the process of claim 1, comprising a drying chamber (3) having an atomizer housing upon which an atomizer wheel (5) is mounted for ejecting droplets of the liquid to be spray dried into the drying chamber, means (2) for providing a stream of drying air

along the outer wall (21) of said housing and surrounding the atomizer wheel (5) and predominantly transversely to the paths in which the droplets are ejected from the wheel, a particle separator (11) for recovering the finest spray dried particles from the drying air, and means for recycling these finest particles to the drying chamber, characterized in that said means for recycling the finest particles comprise at least one pipe (20) debouching in the drying chamber (3) at a location which, when the apparatus is in operation, is within the stream of drying air and upstream of the area where said drying air meets the ejected droplets, and the location for the debouching of said at least one conduit is adjustable to enable adjustment of the distance between the place where the recycled finest particles entrained in drying air collides with the ejected droplets and the atomizer wheel periphery.

3. A spray drying apparatus according to claim 2, wherein the housing is of conical shape having its smallest diameter adjacent to the wheel, and which has a drying air disperser (2) providing a stream of drying air close to the outer walls (21) of said conical housing and in directions parallel thereto, characterized in having the pipe (20) for pneumatic introduction of fine particles to be recycled, passing through said outer wall of the conical housing and which pipe has an aperture (23) into the drying chamber, the rectangular distance (b) of which aperture to the conical outer wall (21) of the housing is adjustable.

4. A spray drying apparatus according to claim 3, characterized in that said rectangular distance (b) from the aperture to the conical wall can be adjusted by telescopic variation of the lenth of an extension (22) of said pipe which projects into the drying chamber.

5. A spray drying apparatus according to claim

4, characterized in that said aperture (23) is placed in a peripheral position near the terminal end of said extension (22), and the extension can due to the telescopic construction be turned to provide further possibility for amending the rectangular distance (b) between the aperture and the conical housing wall (21).

6. A spray drying apparatus according to claim 2, characterized in that the location for the debouching of said at least one pipe is adjustable by means of a swivel joint (25) in that part of the pipe which extends into the drying chamber.

7. A spray drying apparatus according to any of claim 2-4 or 6, characterized in that said at least one pipe (20) is provided with a turnable deflector (26) guiding said finest particles to the periphery of said pipe before discharging them into the drying chamber, which deflector may be turned to pneumatically inject said finest particles in any direction substantially rectangular to the pipe.

8. A spray drying apparatus according to any of the claims 2-7, characterized in having a number selected from 4, 6 and 8 pipes located symmetrically in the same fixed distance from the atomizer axis.

9. A process for spray drying liquids according to claim 1, substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

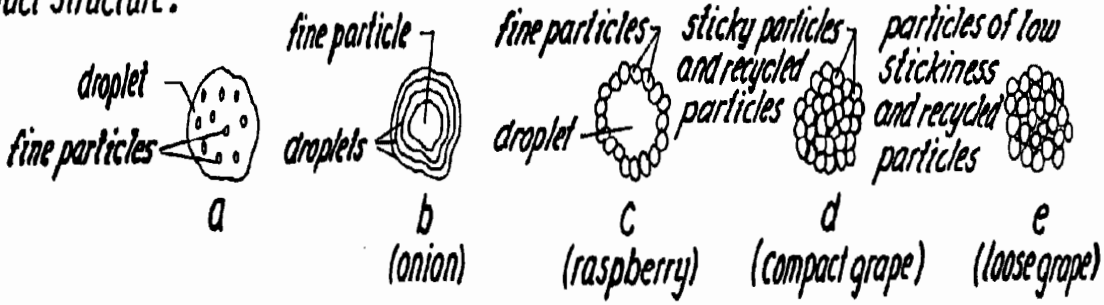
10. A spray drying apparatus according to any preceding claim, substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

F. R. KELLY & CO.,
AGENTS FOR THE APPLICANTS.

Distance between the atomizer wheel and the area where the fine particles are contacted with the droplets or partly dried particles:

short ——————————————— long

Product structure:



Specific bulk volume:

low ——————————————— high

Mechanical stability:

high ——————————————— low

FIG. 1

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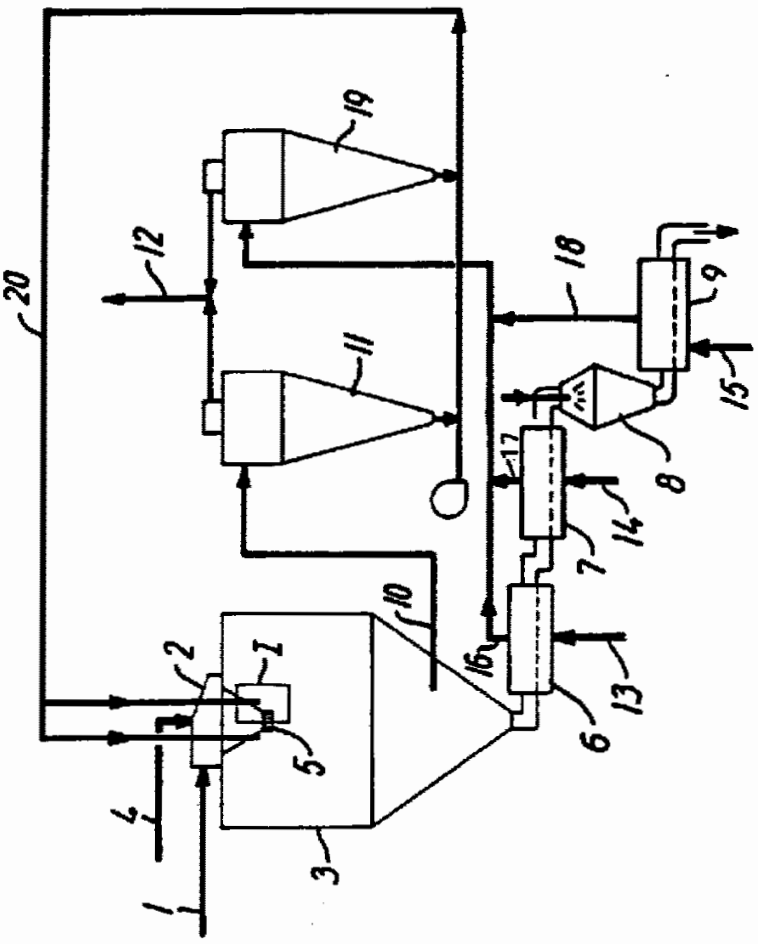


FIG. 2

A/S NIRO ATOMIZER

6 Sheets
Sheet 3

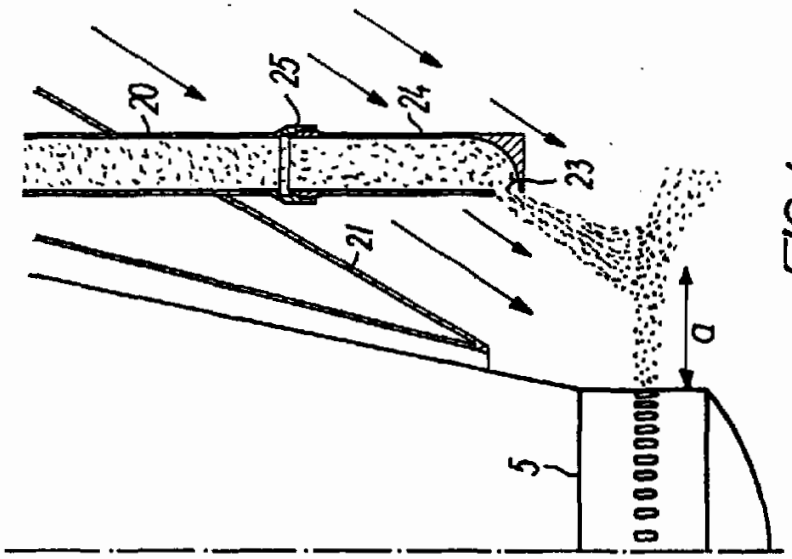


FIG. 4

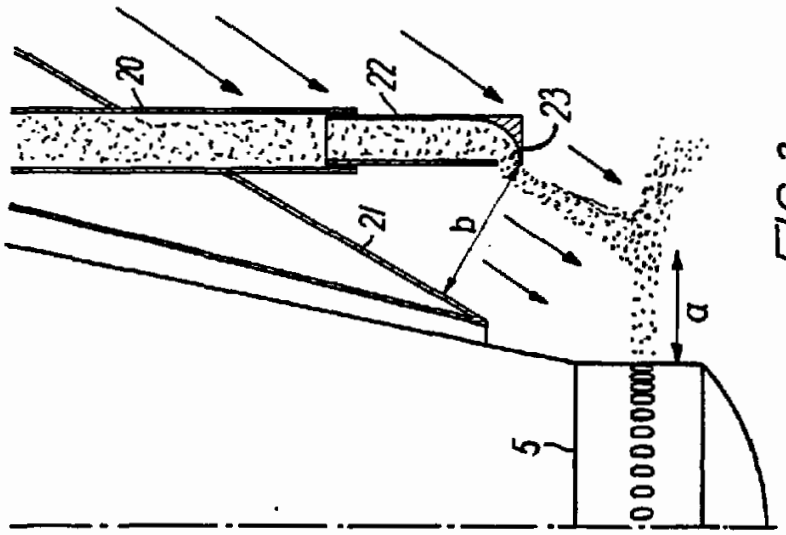


FIG. 3

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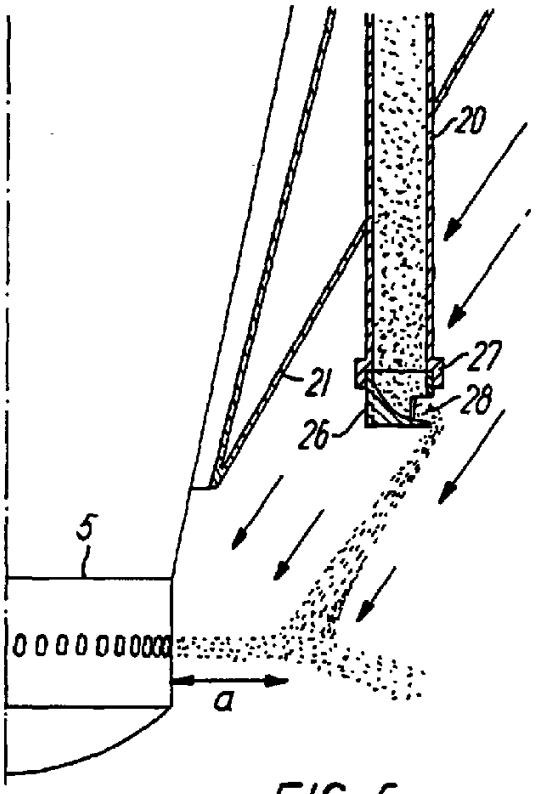


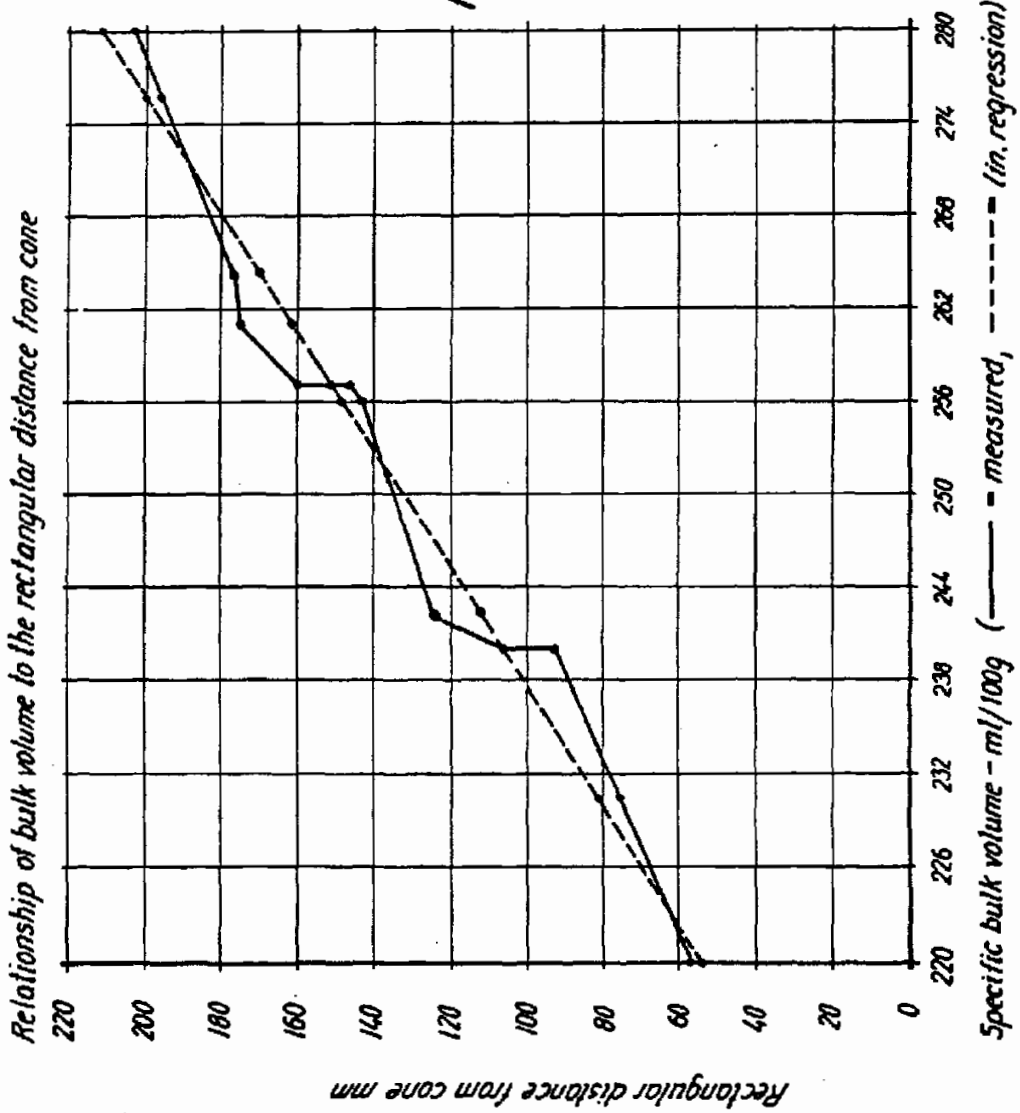
FIG. 5

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A/S NIRO ATOMIZER

6 Sheets
Sheet 5

FIG.6



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A/S NIRO ATOMIZER

6 Sheets
Sheet 6

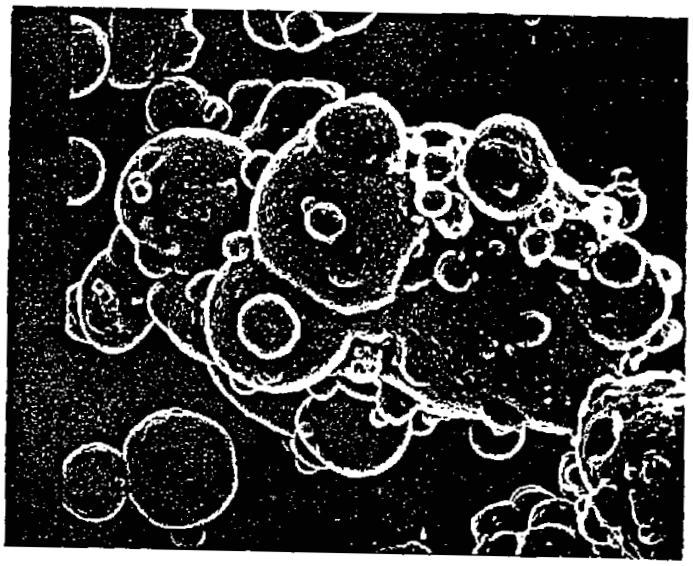


Fig. 7

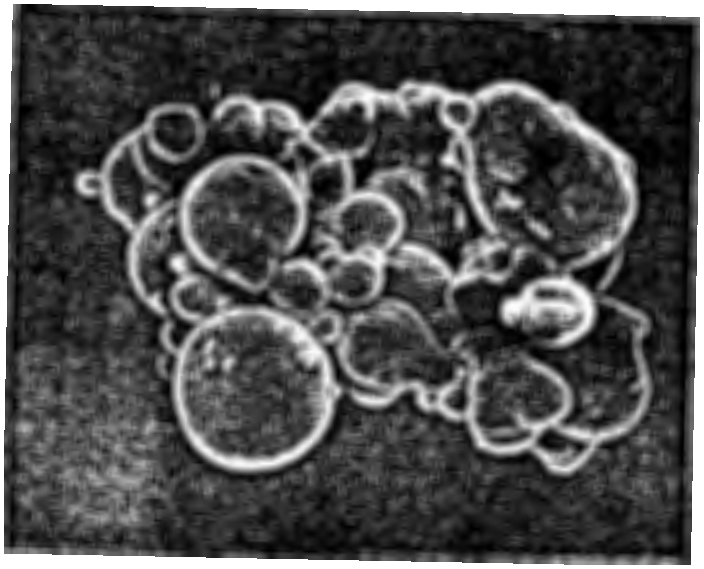


Fig. 8

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(54) Title: FOOD FORTIFIED WITH IRON

(57) Abstract: A fortified foodstuff comprising a fortifying amount of an inorganic compound prepared from sources of ferrous or ferric iron, phosphate and ammonium. These compounds provide an iron fortification system which does not deleteriously affect organoleptic properties of the foodstuff, and which is particularly useful for products containing polyphenols (cocoa, tea, etc.), or which have a high fat content.

FOOD FORTIFIED WITH IRON

FIELD OF THE INVENTION

The present invention relates to the fortification of food and more particularly to the fortification of food with iron.

BACKGROUND OF THE INVENTION

Iron is an essential trace element in animal and human nutrition. It is a component of heme in hemoglobin and of myoglobin, cytochromes and several enzymes. The main role of iron is its participation in the transport, storage and utilization of oxygen.

Deficiency of iron was and remains a common nutritional problem not only in the developing but also in the industrialized countries. Inadequate intake of dietary iron causes the high incidence of anaemia which nutritional surveys have identified among children, adolescents and women. Since the body does not produce minerals, it is totally dependent on an external supply of iron, either nutritional or supplementary. The importance of adequate iron intake is recognized during the whole life of the human being. The recommended daily allowance for iron intake is from 10 to 18 mg per day, and is dependent on age and sex. Children, women up to the time of menopause, and expectant and nursing mothers are in the group with higher requirements of iron.

Iron in the form of a salt or complex can be added to food and/or beverages to provide the daily allowance. The main problems caused by iron sources added to food and beverages are color and off-flavor production, especially in the presence of oxygen, light and at high temperature. Moreover, the addition of iron to beverages, especially to tea, chocolate milk or banana containing drinks, can be very difficult. If highly or slightly soluble sources of iron are used, interaction between the iron and iron sensitive ingredients, such as polyphenols, occurs. Thus, the addition of ferrous sulfate or other soluble iron salts such as ferric sulfate, ferrous lactate, ferrous gluconate, ferrous fumarate, ferric citrate, ferric choline citrate, ferric ammonium citrate, etc., cause chocolate powders and other RTD (ready-to-drink) mixes to turn dark grey when reconstituted with water or milk.

Another problem in iron fortification is the capacity of iron to promote destructive free-radical reactions, which can result in off-flavors. Thus, the addition of soluble iron sources to fat containing products - mostly products

with a high level of unsaturated fatty acids - cause flavor changes due to lipid oxidation. Iron promoted oxidation not only affects the organoleptic properties of foods and beverages, but also undesirably affects the nutritional quality of these products. These interactions can be also enhanced during heat treatment, such as pasteurization or sterilization.

As alternatives to the soluble sources of iron, which are highly bioavailable but lead to an undesirable flavor and/or color, insoluble iron sources such as elemental iron, ferric pyrophosphate, etc. may be used. These forms of iron cause little or no discoloration and off-flavor problems but are poorly bioavailable.

Furthermore, it is well recognized that ferrous compounds in general are more bioavailable than ferric. This correlates with higher solubility of ferrous compared to ferric salts at physiological pH, as well as with lower affinity of Fe(II) to form complexes.

U.S. patent 4,020,158 describes a method of raising the levels of essential bivalent metals in the tissue of animals which comprises the administration to animals of exogenously synthesized metal proteinates by dissolving metal salts in aqueous solutions of protein hydrolysates and adding sufficient base to pH between about 7.5 and 10 to precipitate the metal proteinates. According to the patent only soy protein as source of protein was used to obtain protein hydrolysate (by heating soy protein in hydrochloric acid solution at 130C for 4 hours). Using the complex prepared by this method led to product discoloration when chocolate powders were reconstituted with cold/hot water or milk, indicating weak or incomplete complex formation.

U.S. patent 4,216,144 describes an iron proteinate coordination complex with at least three protein hydrolysate ligands selected from the group consisting of polypeptides, peptides and naturally occurring amino acids. The iron proteinate has been shown by analysis to be at least 70 to 80 percent chelated. Therefore, because of 20 to 30% of free iron, the patented chelate can not prevent discoloration and off-flavor development, particularly when it is used to fortify polyphenol or other fat containing products, such as cocoa, coffee, tea, banana, etc. Thus, improvements in this area are needed.

SUMMARY OF THE INVENTION

We now have developed an iron fortification system which does not deleteriously affect organoleptic properties, and which is particularly useful for products containing polyphenols (cocoa, tea, etc.), or which have a high fat content. This iron fortification system comprises compounds prepared from sources of ferrous or ferric iron, phosphates, and ammonium. Such compounds, on the one hand, possess strong iron-ligand bonds which prevent reactivity of free iron and, on the other hand, dissociate at the acidic stomach media to provide high bioavailability of iron.

Accordingly, the present invention provides a fortified foodstuff comprising a fortifying amount of an inorganic compound prepared from sources of ferrous or ferric iron, phosphate and ammonium.

DETAILED DESCRIPTION OF THE INVENTION

Advantageously, the foodstuff which is to be fortified with iron is a food or beverage, particularly a food or beverage that is sensitive to oxidation, off-flavor development, or discoloration in the presence of free iron.

The foodstuff may be a dairy-based product such as a milk cocoa containing beverage, a liquid nutritional product or other beverages such as a juice, or it may be a powdery product, e.g., instant coffee, cocoa containing mixtures (e.g, MILO, NESQUIK, etc.) liquid formulae, and the like.

The developed ferrous and ferric compound also work well in fortified products containing iron-sensitive components, such as polyphenols, unsaturated fatty acids, etc.

The amount of iron provided in the food or beverage may be from 1 to 200ppm, preferably from 5 to 100ppm and more preferably from 10 to 75ppm.

The iron ferrous source that can be used to create these compounds can include any food grade ferrous salt, such as ferrous sulfate, ferrous ammonium sulfate, ferrous chloride, ferrous malate, ferrous acetate, ferrous gluconate, ferrous nitrate, ferrous lactate, ferrous fumarate, ferrous succinate, and ferrous oxide, ferrous hydroxide or mixture thereof. The most preferred material is ferrous sulfate.

The iron ferric source that can be used to create these compounds can include any food grade ferric salt, such as ferric sulfate, ferric chloride, ferric nitrate, ferric acetate, ferric malate, ferric ammonium acetate, ferric formate,

ferric oxide, ferric hydroxide or mixture thereof. The most preferred of these is ferric sulfate.

Elemental iron also can be used as iron source to create these compounds.

The source of phosphates that can be used to create these compounds can include any food grade orthophosphate salt, such as mono-, di or tri-sodium, potassium, ammonium, magnesium or calcium phosphates, as well as phosphoric acid, or mixture thereof. Preferably, phosphoric acid is used.

The source of ammonium that can be used to create these compounds can include any food grade ammonium source, such as ammonia water, ammonium hydroxide, ammonium acetate, ammonium bicarbonate, ammonium carbamate, ammonium carbonate, ammonium chloride, ammonium lactate, ammonium sulfate, ammonium ferrous sulfate, ammonium ferric sulfate, ammonium nitrate, mono-, and di-basic ammonium phosphates, or mixture thereof. Preferably, ammonium hydroxide is used.

The inorganic compounds, which are the object of this invention, may conveniently be formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates (phosphoric acid or phosphate salt with any of the abovementioned acids), and then with any suitable source of ammonia. For example, the inorganic compounds may be formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates under acid conditions and then adjustment of the pH of the compounds with any suitable source of ammonia. The acid that can be used to create these compounds is not limited and may be any of a number of food grade inorganic or organic acids such as phosphoric, hydrochloric, sulfuric, acetic, lactic, malic, nitric, fumaric, gluconic, succinic, ascorbic or mixture thereof. The most preferred acid is phosphoric acid.

Most preferably, the compounds may be prepared by combining ferrous or ferric sulfate with phosphoric acid under agitation, and then adjusting pH to about 5.5 - 9 by addition of ammonium hydroxide. The preferable pH range is about 6 - 7.5, and the most preferred is 6.5 - 7. The weight ratio between the iron, ammonia, and phosphate groups may be 1: (0.2 - 5) : (0.4 -10), preferably 1: (0.6 - 3) : (2.5-8.5), and most preferably 1: (0.8 - 1.75) : (3.5 - 5).

In the presence of the essential amount of ammonia, a food grade alkaline agent may be used for pH adjustment, including but not limited to

sodium hydroxide, potassium hydroxide, ammonia hydroxide, magnesium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate or mixture thereof.

Advantageously, the iron containing compound may be added to the foodstuff in a form of an aqueous dispersion or as a dry powder.

The inorganic compound prepared from sources of ferrous or ferric iron, phosphate and ammonium may be used to fortify beverages and foods giving improved palatability without affecting product quality.

The preferred iron compound is the ferrous compound which not only possesses strong functional properties similar to the ferric compound in preventing iron reactivity, but also has very high free iron release at stomach pH (i.e., close to that of ferrous sulfate), so its high bioavailability can be achieved. The ferrous compound has good functionality to prevent discoloration, off-flavor, and fat oxidation, together with high iron release at stomach pH.

Based on analytical data of elemental (Fe, N, P) analyses and ionic HPLC, the chemical formula of the inorganic ferrous compound formed by the interaction of ferrous, phosphates and ammonium sources was determined as $FeNH_4PO_4$. The level of the iron load in the compound was determined to be very high (30-32%). These compounds can be dried by means known to those skilled in the art. This can include filtration, freeze or spray drying. The dried products are readily dispersible in water.

The fortified foodstuff comprising a fortifying amount of ferrous ammonium phosphate may be prepared by forming this inorganic compound and by adding the compound to the foodstuff. The foodstuff can then be heat-treated by normal means without any loss in quality such as discoloration, lipid oxidation, or fouling of processing equipment. The resulting fortified foodstuff is similar to its non-fortified counterpart in organoleptic quality such as flavor, aroma, color, texture, viscosity or mouthfeel.

The invention provides the following improvements and advantages.

1) the ferrous and ferric ammonium phosphate compounds are very effective in fortifying food and beverages, particularly those containing polyphenols and/or unsaturated fat, which are sensitive to discoloration and off-flavor development in the presence of free iron.

2) the compounds are easy to produce.

3) the level of iron load in the compounds is very high, e.g., 30-32%, for ferrous ammonium phosphate.

4) due to rapid and high iron release at stomach conditions (at a pH of between 2 and 3.5), the good bioavailability of ferrous ammonium phosphate could be assumed.

5) no allergenicity of the ferrous and ferric ammonium phosphate compounds could be assumed due to their inorganic nature.

EXAMPLES

The following examples further illustrate the present invention. Parts and percentages are given by weight unless otherwise stated.

Example 1. Preparation of inorganic iron compound

58 grams of phosphoric acid (85%) was dissolved in 1 liter of distilled water. Ferrous sulfate heptahydrate was added (56 g) and then pH was adjusted to 6.8 with ammonium hydroxide (28%). Precipitates, formed during neutralization, were separated by filtration (Whatman, 42), then carefully washed with de-ionized water and dried under air at room temperature.

Example 2. Preparation of inorganic iron compound with different order of ingredient addition

58 grams of phosphoric acid (85%) was dissolved in 1 liter of distilled water. Ferrous sulfate heptahydrate was added (56 g) and then pH was adjusted to 6.8 with ammonium hydroxide (28%). Precipitates, formed during neutralization, were separated by filtration (Whatman, 42), then carefully washed with de-ionized water and dried under air at room temperature.

Example 3. Preparation of inorganic iron compound in spray dried form

58 grams of phosphoric acid (85%) was dissolved in 1 liter of distilled water. Ferrous sulfate heptahydrate was added (56 g) and then pH was adjusted to 6.8 with ammonium hydroxide (28%). The liquid was spray dried using atomizing spinning disk spray-drier (T_{in} = 145C, T_{out} = 80C).

Example 4. MILO and NESQUIK powder fortification.

Iron compounds (ferrous ammonium phosphate) from Examples 1, 2 and 3 were added to 22.0 g of MILO powder (a commercial product sold by Nestlé whose ingredients are sugar, skimmed milk powder, glucose syrup, palm fat, cocoa and permitted food conditioner) and NESQUIK powder (a commercial powdered chocolate flavor sold by Nestlé whose ingredients are sugar, cocoa, soy lecithin, salt, artificial and natural flavor). These chocolate powders were then reconstituted with 180 ml of boiling water or milk, respectively (15.0 ppm final iron concentration). Products were stirred briefly and allowed to stand for

15 minutes at room temperature. After 15 minutes, products were judged by a taste panel of 10 people.

The results of the effect of iron fortification are presented in Table 1. It has been found that the ferrous compound diminishes cocoa discoloration when iron fortified (15 ppm) NESQUIK powder was reconstituted with boiling water or milk. Color changes presented by its total color difference, DE, are shown in Table 1, where DE is calculated from the Hunter equation:

$$\Delta E = (L_i - L_{control})^2 + (a_i - a_{control})^2 + (b_i - b_{control})^2$$

Thus, as shown in Table 1, minor color changes were determined in MILO or NESQUIK powders that were fortified with the novel ferrous compound as compared to products fortified with ferrous sulfate, which produced a significant color change. Significantly less differences were observed when reconstituted with cold water or milk. The iron fortified NESQUIK powder reconstituted with boiling milk and MILO powder reconstituted with boiling water were judged by 10 panelists. No off-flavor and visual performance were found in NESQUIK and MILO samples fortified with the novel ferrous or ferric inorganic compound as compared to the control without added iron.

Table 1. Effect of iron fortification on discoloration of cocoa containing products

additive	MILO powder (ΔE)	NESQUIK powder (ΔE)
$FeHN_4PO_4$	1.1	1.5
commercial $Fe(PO_4)_2$	1.1	1.4
$FeSO_4$	10.5	10.3
control (no additive)	0.2	0.2

Example 5. MILO powder beverage fortification

Iron compound from Examples 1, 2 and 3 were added to chocolate milk (8.5% MILO powder, 15 ppm total iron). Iron fortified MILO chocolate milk was autoclaved at 121°C for 5 min in 125 ml glass jars, closed and cooled to room temperature. Autoclaved and Ultra high temperature ("UHT") sterilized samples were evaluated for color and taste after 1 month storage at ambient temperature. No color changes and off flavors were found when samples were compared to control samples without added iron, while samples fortified with ferrous sulfate turned dark gray and had off-flavor.

Example 6. Lipid oxidation

Fish oil contains a substantial amount of polyunsaturated fatty acids, which make it highly susceptible to oxidation. It is known that binding of free iron reduces iron pro-oxidant activity. To prove this, the extent of lipid oxidation and induction time thereof was measured by conductivity changes using a Metrohm Rancimat, model 617.

Ferrous ammonium phosphate was added to fish oil. The same amount of iron, as ferrous sulfate, was also added to a second sample of fish oil. Both samples along with a control sample (without added iron), were heated at 100C and induction time was determined using the Rancimat. No difference in oxidation induction time was found between the fish oil fortified with ferrous ammonium phosphate and the control sample without added iron. However, induction time of fish oil fortified with ferrous sulfate was about 50 - 60 % less

than the other two samples. Therefore, the results of a rancidity test (see Table 2) showed that the presence of 50 ppm ferrous ammonium phosphate $FeHN_4PO_4$, prevents fish oil oxidation caused by iron.

To compare, the induction time for fish oil fortified with ferric sulfate was about 60% less than the control (i.e., no additive). Similar results to ferrous ammonium phosphate were obtained for ferric ammonium phosphate.

Further, no lipid oxidation as compared to control with no added iron was found by measuring hexanal level in headspace of instant liquid formula samples fortified with ferrous ammonium phosphate (50 ppm iron) after incubation for 3 days at 60C. However, a high hexanal level of 3.5 ppm was detected in ferrous sulfate containing sample, indicating lipid oxidation in the product (see Table 2).

Table 2. Effect of iron fortification on lipid oxidation

additive	induction time (hr.)	hexanal measured (ppb)
$FeHN_4PO_4$	6.1	30
commercial $Fe(PO_4)_2$	6.0	32
$FeSO_4$	2.5	3500
control (no additive)	6.0	40

Example 7

To estimate the bioavailability of ferrous ammonium sulfate ($FeHN_4PO_4$) the iron release at conditions similar to the adult and infant stomach (37C, pH = 2.0 and 3.5 by HCl, respectively) were determined. Rapid and high iron release (90 to 100% of the total iron) were observed at both pH 2 and pH 3.5.

THE CLAIMS

What is claimed is:

1. A fortified foodstuff comprising a fortifying amount of an inorganic compound prepared from sources of ferrous or ferric iron, phosphate and ammonium.

2. A fortified foodstuff according to claim 1 wherein the foodstuff which is fortified is a food or beverage that is sensitive to oxidation, off-flavor development, or discoloration in the presence of free iron.

3. A fortified foodstuff according to claim 1 wherein the foodstuff which is fortified is a milk cocoa containing beverage, a liquid nutritional product, a juice, or a powdery product.

4. A fortified foodstuff according to claim 1 wherein the foodstuff which is fortified is instant coffee, a cocoa containing mixture, or a liquid formula in powdered form.

5. A fortified foodstuff according to claim 1 wherein the fortifying amount of iron in the food or beverage is from about 1 to 200ppm.

6. A fortified foodstuff according to claim 1 wherein the iron ferrous source used to create the inorganic compound is ferrous sulfate, ferrous ammonium sulfate, ferrous chloride, ferrous acetate, ferrous malate, ferrous citrate, ferrous gluconate, ferrous nitrate, ferrous lactate, ferrous fumarate, ferrous succinate, ferrous oxide, ferrous hydroxide or a mixture thereof.

7. A fortified foodstuff according to claim 1 wherein the iron ferric source used to create the inorganic compound is ferric sulfate, ferric chloride, ferric nitrate, ferric acetate, ferric ammonium acetate, ferric formate, ferric oxide, ferric hydroxide or a mixture thereof.

8. A fortified foodstuff according to claim 1 wherein the iron source used to create the inorganic compound is elemental iron.

9. A fortified foodstuff according to claim 1 wherein the source of phosphate used to create the inorganic compound is mono-, di or tri-sodium, potassium, ammonium, magnesium or calcium phosphate, phosphoric acid, or a mixture thereof.

10. A fortified foodstuff according to claim 1 wherein the source of ammonium used to create the inorganic compound is ammonia water, ammonium hydroxide, ammonium acetate, ammonium bicarbonate, ammonium carbamate, ammonium carbonate, ammonium chloride, ammonium lactate, ammonium sulfate, ammonium ferrous sulfate, ammonium ferric sulfate, ammonium nitrate, mono-, and di-basic ammonium phosphates, or a mixture thereof.

11. A fortified foodstuff according to claim 1 wherein the inorganic compound is formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates and with any suitable source of ammonia.

12. A fortified foodstuff according to claim 1 wherein the inorganic compound is formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates under acid conditions and then adjustment of the pH of the compounds with any suitable source of ammonia.

13. A fortified foodstuff according to claim 12 wherein the acid used to create the inorganic compound is phosphoric, hydrochloric, sulfuric, acetic, lactic, malic, citric, nitric, fumaric, gluconic, succinic, ascorbic or a mixture thereof.

14. A fortified foodstuff according to claim 12 wherein the inorganic compound is prepared by combining ferrous or ferric sulfate with phosphoric acid under agitation, and then adjusting pH to 5.5 - 9 by addition of ammonium hydroxide.

15. A fortified foodstuff according to claim 11 wherein the weight ratio between the iron, ammonia , phosphate groups of the compounds is 1: (0.2 - 5) : (0.4 : 10).

16. A fortified foodstuff according to claim 11 wherein the inorganic compound is $FeNH_4PO_4$.

17. A fortified foodstuff according to claim 11 wherein, in the presence of ammonia, pH adjustment of the inorganic compound is carried out by adding sodium hydroxide, potassium hydroxide, ammonia hydroxide, magnesium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate or a mixture thereof.

18. A fortified foodstuff according to claim 1 wherein the inorganic compound is provided in dry form by filtration, freeze or spray drying.

19. A process of preparing a fortified foodstuff according to claim 1 which comprises adding the compound to the foodstuff in a form of an aqueous suspension or as a dry powder.

20. A process of preparing a fortified foodstuff according to claim 19 wherein the inorganic compound is formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates and with any suitable source of ammonia.

21. A process of preparing a fortified foodstuff according to claim 19 wherein the inorganic compound is formed by the interaction of a suitable iron source (II or III) with a suitable source of phosphates under acid conditions and then adjustment of the pH of the compounds with any suitable source of ammonia.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/00619

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/304 A23L2/52 A23C9/152 A23C9/13 A23G1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23L A23C A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, FSTA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	page 7, line 20 -page 8, line 3	9,15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Form PCT/ISA/210 (second sheet) (July 1992)

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(54) Title: EGG-BASED POWDER AND FOOD CONTAINING THE SAME

(57) Abstract: An egg-based powder is made available as a gelling and emulsifying component in fermented foods of the drinks, dessert, fromage frais and set or creamy yoghurt type and is remarkable in that the entire properties of the eggs are preserved while ensuring the absence of salmonella by using only natural components.

Egg-based Powder and Food Containing the Same

The invention relates to a pasteurized egg-based powder whose organoleptic and functional properties are similar to those of egg after reconstituting in an aqueous medium.

It also relates to an egg-based fermented food of a novel type, manufactured from such a composition.

Eggs are often used for their excellent functional properties, for example their gelling and emulsifying properties, for their colour and for their taste. It is known that egg-based food products are not free of microbiological risks since eggs may contain sporulated microorganisms and salmonella. Egg proteins usually lose their functional properties, in particular their gelling ability, under the heat treatment conditions which would be necessary for the elimination of resistant spores and salmonella. Accordingly, industrial egg products are generally pasteurized, which does not eliminate all risks. Because of residual risks, the use of eggs is limited. In particular, the use of eggs which have been simply pasteurized in a conventional manner under conditions which maintain their organoleptic and functional properties would not be possible in food products which have to undergo fermentation.

A spray-dried composition based on egg and skimmed milk capable of being reconstituted in water is known for example from FR-A-2 118 688. This composition results from drying a mixture of whole egg and skimmed milk which have been separately pasteurized. In particular, the egg is heat-treated at 64.5°C/2 min 1/2, which does not make it possible to ensure complete absence of salmonella. That is not essential in the context of this document since the egg/milk powder is intended for use in cakes which are manufactured by prolonged baking of the mix at high temperature. This composition cannot be used in uncooked food products, for example, dairy products.

A fermented drink based on milk and egg is also known for example from FR-A-2 737 643. Such a drink is manufactured by preparing a liquid egg mixture which has been highly diluted in water, supplemented with skimmed milk powder, glucose and fructose, the content of egg not exceeding 10% in the mixture, heat

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treatment by pasteurization, cooling followed by lactic acid fermentation of the mixture thus treated. This product is not based on a powder and the egg is treated with a high temperature while being strongly diluted in water.

It is for example known from EP-A-0 820 704 that it is possible to sterilize a mixture of milk, egg and sugar by the liquid route and, where appropriate, drying the mixture, thereby losing the functional properties of the egg and using the gelling properties of the casein in the presence of calcium under the effect of heat to replace the functional properties of the egg which are lost during the hygienization heat treatment. The re-established gelling properties of the system are exploited to manufacture desserts of the flan type.

The problem forming the basis of the present invention is the making available of a product based on whole egg, which would have the desired functionality, in particular the emulsifying ability and the gelling capacity, which could be used in the preparation of food products while being hygienic and in particular which would be suitable for the preparation of dairy food products.

There is also a need for an easy to use texturising powder, which has a natural image, the advantage of egg, and which is safe to use in all food products including uncooked foods.

The invention relates to a texturizing powder suitable for use in cooked and uncooked food products, comprizing a pasteurised mixture of non-coagulated egg and milk protein; the mixture being pasteurised at a temperature above 65°C.

In another aspect, the present invention relates to a texturizing powder for a food product comprising:
a milk protein component, and an egg component,
the components being pasteurized, in the form of a mixture, so as to eliminate bacteria,
the mixture being dried,
and the powder retaining the functional and organoleptic properties of the egg once reconstituted in an aqueous medium.

In a third aspect, the present invention relates to a texturizing powder comprising egg and milk protein, the powder obtainable by creating a mixture of egg and milk protein,
pasteurizing the mixture at a temperature above 65°C,
drying the mixture.

The powder is stable for a long period from the microbiological point of view and has the property of not being susceptible to recontamination as would be the case for a composition in liquid form. Furthermore, there is no phase separation or settling out during storage or upon reconstitution.

Without wishing to be bound by theory it is postulated that the milk or whey proteins protect the egg proteins from coagulation at a temperature above 64°C. This protection may account for the ability to conduct a pasteurization even above 70°C, which means that hygiene criteria for many uncooked products are met, while at the same time the functional properties of egg are not lost.

In another aspect, the present invention relates to a food product or a beverage, which contains the powder.

The present invention also relates to a chilled dairy product, which contains pasteurized eggs as a texturizing agent and which has the same organoleptic properties of a product containing fresh eggs.

In a further aspect, the present invention provied a process for preparing a powder, in which a concentrated lactic base rich in whey protein or in leguminous plant protein, and liquid egg is mixed, and then the mixture is pasteurized by heat treatment at above 65°C while preserving the organoleptic and functional properties of the egg and it is dried.

In another aspect, the present invention provides a process for manufacturing a chilled dairy product, in which a mixture of whole milk or milk which has been skimmed to a greater or lesser degree, carbohydrates and the powder set out above is prepared by dissolution and the mixture is treated by lactic acid fermentation.

In another aspect, the present invention relates to the use of the powder described above as a replacement for egg in an egg-based product.

Preferably, the powder is obtained without addition of stabilizing or emulsifying additives, and without adding water before pasteurization.

Preferably, the powder is easily reconstitutable in water.

Preferably, the dry weight ratio of egg to milk protein in the powder is 0.5:1 to 1.5:1, more preferably 0.8:1 to 1.2:1. If the milk protein is whey protein, the powder preferably comprises 35 to 55% of whey protein and 45 to 65% by weight of egg, with respect to dry matter. More preferably, it comprises 40 to 50% whey protein and 50 to 60% of egg.

The milk proteins are preferably derived from a whey concentrate containing 35 to 80% by weight of proteins. Such a concentrate is advantageously obtained from the ultrafiltration or the microfiltration of sweet or acid whey from casein making or from cheese making.

Preferably, pasteurization temperature is above 65°C, preferably above 67°C, even more preferably above 70°C, 72°C, 74°C or 76°C. For example, the pasteurization temperature is between 70 and 75°C. In an embodiment, the pasteurization temperature is between 65°C and 78°C, preferably between 70 and 76°C, most preferably between 72 and 76°C.

The egg preferably is low temperature pasteurized whole egg.

Low temperature pasteurization of egg, in the context of the present invention, refers to a pasteurization temperature, which is equal to or lower than 65°C. In general, it refers to a temperature at which the egg proteins contained in egg do not coagulate. For undiluted eggs or eggs not supplemented by additives this temperature is considered to be around 65.5°C.

Preferably, at least 30% by weight of the dry matter content of the powder is derived from whey.

The invention also relates to a process for preparing a product above, in which a concentrated lactic base rich in whey protein or in leguminous plant protein, and liquid egg is mixed, and then the mixture is pasteurized by heat treatment at above 65°C while preserving the organoleptic and functional properties of the egg are the mixture is dried.

In an embodiment of the process, in which the egg component and the lactic base are mixed, the pH is adjusted, where appropriate, to a value ranging from 6.5 to 7.5, and the mixture is then pasteurized at a temperature of at most 78°C for 10-20 s.

In the context of the invention, the expression lactic base rich in whey protein is understood to mean any raw material of lactic origin containing lactic proteins, rich in serum proteins, in particular in lactalbumins. It is possible to use any raw material containing whey proteins in concentrated form, for example an acid whey from casein making or a sweet whey from cheese making, obtained by separating the curd containing the casein, preferably concentrated by ultrafiltration or microfiltration, followed, where appropriate, by diafiltration (ultrafiltration with washing with water). The concentrate may be demineralized or made lactose free to a greater or lesser degree.

As a variant, it is possible to use, as source of lactic protein, a vegetable milk, for example a soyabean milk, concentrate or isolate, with a high concentration of proteins. Equally, the milk protein may be replaced by meat protein.

The liquid egg which may be used in the process of the invention may be a mixture of egg yolk and egg white, or preferably a whole egg in liquid form, which has been pasteurized beforehand. It is possible to use fresh egg, ripened egg, that is to say which has been stored at refrigeration temperature, for example at about 4°C, for a period of up to several days, a mixture of egg white and egg yolk having been ripened separately, whole egg enriched with egg yolk or with egg white, all these raw materials having been separately pasteurized.

To carry out the process, the undiluted egg component and the milk protein component are mixed, with stirring, the pH is adjusted, where appropriate, to a

value ranging from 6.5 to 7.5, and then the mixture is preheated, for example using a plate exchanger, preferably at a temperature of less than or equal to 75°C.

The pasteurization treatment may be carried out in an indirect manner by means of a plate exchanger. As a variant, it is possible to carry it out in a jacketed holding unit. The pasteurization should be carried out under conditions which are lethal for salmonella while making it possible not to coagulate the egg, in short to preserve its functional qualities, in particular its emulsifying and gelling powers, and its organoleptic qualities, in particular its taste and its colour. It takes place preferably at a temperature of at most 76°C for 10-20 s.

The mixture in question is then dried, for example spray-dried in a drying tower under moderate to medium conditions.

Once dried, and where appropriate supplemented with other dehydrated ingredients of the recipe, the mixture may be reconstituted with an aqueous medium and then subjected to subsequent treatment for preparing an egg-based food as a replacement for egg.

Thus, the powder according to the invention may be used as a basic ingredient in any food comprising the use, in the form of a mixture, of milk, egg and carbohydrates with the aim of forming a gel upon cooking. There may be mentioned savoury culinary preparations for flan, omelettes, quiches or sauces, or sweetened preparations for pastry, in particular for cakes, creams or flans.

The invention also relates to a food product or a beverage, which contains the powder described above.

The invention also relates to a chilled dairy product, which contains pasteurized eggs as a texturizing agent and which has the same organoleptic properties of a product containing fresh eggs.

In an embodiment, the product is free of other gelifying and texturizing agents, additives, hydrocolloids or gelatine.

The invention also relates to dairy product containing egg, chosen from milk drinks, yoghurts and desserts, containing 0.5 to 10% by weight of a powder above.

The product may be in the form of a gelled dessert of the flan or mousse type. It may be in the form of set or creamy yoghurt. It may also constitute an acid drink.

The product may also be a fromage frais.

In an embodiment, the food product is a mayonnaise.

The invention also relates to a process for manufacturing a fermented food product above, in which a mixture of whole milk or milk which has been skimmed to a greater or lesser degree, carbohydrates and powder described above is prepared by dissolution and the mixture is treated so as to form a gel by lactic acid fermentation.

It is possible to start with fresh milk, standardized by adding cream or vegetable fat. It is also possible to start with milk reconstituted from skimmed milk powder and anhydrous lactic fat.

The carbohydrates which may be used in the above process are in particular sucrose and lactose, when it is desired to use the product according to the invention to manufacture a sweetened food, alone or in the form of a mixture. The carbohydrates represent 3 to 20% and preferably about 10% by weight of the mixture.

After dissolution, the mixture may be pasteurized, for example at 90-105°C for 2 to 10 min, cooled to about 70-75°C and then homogenized in a 1 or 2-stage homogenizer, preferably, for a single stage, at a pressure of 75 to 300 bar, or for two stages, at pressures of 75/15 bar to 300/60 bar, and then cooled to a temperature, chosen for the fermentation, of 25 to 45°C.

The fermentation is carried out in a conventional manner. To do this, it is possible to use lactic ferments in yoghurt and/or in fromage frais, where appropriate with probiotic ferments.

A gel may be prepared which may constitute the final fermented product. It is also possible to smooth the fermented mass or to give it a degree of overrun.

The fermented product thus obtained may constitute the final product or may constitute a fermented filling, where appropriate in the presence of other components as receptacle, inclusions, accessories or flavouring ingredients.

The heat treatment for pasteurizing the eggs in the form of a mixture with the milk proteins does not destroy the functional properties of the egg proteins. Thus, the preparation of a food, for example a flan or a mousse, remains possible by virtue of the exploitation of the gelling properties and of the overrun and emulsifying capacity of the egg proteins. In particular, the powder according to the invention is suitable for conventional cooking in a hot air oven or even for indirect sterilization in a heat exchanger, for example at 120-125°C/20 s in the presence of the other ingredients of the dessert.

If a mayonnaise is produced, the powder according to the present invention may replace part or all of the egg in the mayonnaise. Any mayonnaise may be produced with the powder, for example 80% fat, 50% or 35 % fat (in percent by weight). The contents of all ingredients may therefore be varied according to personal gusto.Usually, all ingredients of the mayonnaise, including the powder, are mixed and the oil is emulsified in, which may be by batch wise operating emulsifyer machines, with continous emusifyer machines or with colloid mills. Different oil-drop sizes may be optained by this process, for example 3 to 10 µm.

If the fat content is desired to be lower, there are usually thickeners mixed separately in an aquous solution, heated and finally introduced into the basic mayonnaise as obtained above. In general, the same recipies like known may be used and the classic egg powders are just partially or totally replaced by the powder according to the present invention.

The examples below illustrate the invention. In these examples, the parts and percentages are by weight, unless otherwise stated.

Example 1

Preparation of a powder

A sweet whey concentrate from cheese making, obtained from ultrafiltration and containing 35% of protein, is dissolved in water and liquid whole egg, pasteurized beforehand, is added in a tank, with stirring, so as to obtain 55.5% egg dry matter content per 44.5% whey dry matter content.

After having adjusted, where appropriate, the pH to a value of 6.8 to 7.2 by adding a food grade concentrated aqueous sodium hydroxide solution, the mixture is pumped, by means of a positive pump, to a plate exchanger where it is heated to 72°C and maintained at this temperature for 15 s; it is cooled to 60°C and then it is spray-dried in a drying tower in an air stream, the hot air admission temperature being 190°C and the air outlet temperature 92°C.

Example 2

Preparation of a filling for quiche

The powder of Example 1 is used by dissolving it in an amount of 3.5% in 87.5% whole milk and adding 9% sucrose, as a base for producing a quiche Lorraine. After baking in an oven in a conventional manner, the texture and the taste of the quiche are similar to those of a traditional quiche.

Example 3

Preparation of a fermented dessert flan

The powder of Example 1 is used by dissolving it in an amount of 2.88% in 84.6% whole milk and adding 8.72% sucrose. After pasteurizing at 105°C/2 min, the mixture is cooled to 45°C and homogenized in a 2-stage device at an overall pressure of 300 bar, and it is then cooled to 40°C. It is inoculated with 3.8% of a mixture of ferments for yoghurt and it is incubated at 40°C until a pH of 4.7 is obtained. The product thus obtained is cooled in a cold chamber at 4-6°C and stored at this temperature. After cooling, the firmness of the gel is totally comparable to that of a home-made flan obtained conventionally from fresh eggs.

Example 4

Preparation of a stirred yoghurt

The powder of Example 1 is used by dissolving it in an amount of 3.42% in 84.12% of whole milk and by adding 8.66% sucrose. After pasteurizing at 105°C/2 min, the mixture is cooled to 45°C and homogenized in a single-stage device at 300 bar, and it is then cooled to 40°C. It is inoculated with 3.8% of a mixture of ferments for yoghurt and incubated at 40°C until a pH of 4.6 is obtained. The fermented mixture is then smoothed, cooled to 6°C and poured into pots which are sealed.

Example 5

Preparation of an egg-based fermented drink

The powder of Example 1 is used by dissolving it in an amount of 2.48% in 80.85% of water and adding 8.2% of sucrose, 7.07% of powdered skimmed milk and 1.38% of anhydrous lactic fat. After pasteurizing at 105°C/2 min, the liquid is cooled to 75°C and the mixture is homogenized in a 2-stage device at an overall pressure of 300 bar and it is then cooled to 40°C. It is inoculated with 0.02% of a thermophilic lactic ferment for yoghurt and incubated at 40°C until a pH < 5 is obtained; the curd mass is smoothed and cooled to 6°C. Pots are then filled and sealed in a traditional manner.

Example 6

Preparation of a gelled fermented milk

A fatty gelled fermented milk of the yoghurt type enriched with probiotic bacteria is prepared. 89.3 parts of milk respectively containing 30 g/l of lactic fat are mixed with 3.7 parts of powder of Example 1 and the mixture is preheated to 70°C; it is pasteurized at 92°C/6 min and then, after cooling to 70°C, it is homogenized in a single-stage device at 300 bar. After cooling to 43°C, the mixture is inoculated with 2% of a common yoghurt starter Streptococcus thermophilus and Lactobacillus bulgaricus, to which 5% of Lactobacillus

johnsonii (La1, CNCM I-1227) is added. After packaging in pots, the fermentation is carried out at 38°C until a pH of 4.6 is obtained, and then cooled to 6°C.

Example 7

Preparation of a dessert mousse

A pasteurized base which can be caused to acquire a degree of overrun, consisting of a mixture of lactic proteins, sugar, powder of Example 1, chocolate and cocoa, is prepared so as to manufacture a chocolate mousse, starting with the ingredients and in the proportions indicated in Table 1 below.

Table 1

Ingredients	**%**
Whole milk or skimmed milk or water	57.8
Powder according to Example 1	4.6
Sucrose	14.6
Dark chocolate and alkalized chocolate	21
Cocoa powder	2

The ingredients are mixed, they are preheated to 70°C and then they are heat-treated by UHT with direct injection of steam at 143°C/10 s. After cooling by expansion under vacuum at 70°C, and then by plate exchanger at 10°C, the mixture is aerated in a Mondomix® apparatus for producing overrun until an overrun of 75-100% by volume is obtained.

Example 8

Preparation of a mayonnaise

An 80% fat mayonnaise (percent by weight) is prepared by mixing and stirring all ingredients but oil present in table 2 below. Then oil is emulsified in continuously

with a roto/strato emulsifyer machine. In so doing, a mayonnaise with a mean oil drop size of 3 – 10 μm is achieved.

Table 2

Ingredients for preparation of a 80%-fat mayonnaise

Ingredients	**%**
Water	8.6025
Salt	1.1000
Spirit vinegar 11%	2.700
Lactic acid 88%	0.7780
Sunflower oil	80.000
Egg – milk powder from example 1	4.000
Flavour, spices	2.8195

Claims

1. A texturizing powder suitable for use in cooked and uncooked food products, comprizing a pasteurised mixture of non-coagulated egg and milk protein; the mixture being pasteurised at a temperature above 65°C.

2. A texturizing powder for a food product comprising:
a milk protein component, and an egg component,
the components being pasteurized, in the form of a mixture, so as to eliminate bacteria,
the mixture being dried,
and the powder retaining the functional and organoleptic properties of the egg once reconstituted in an aqueous medium.

3. A texturizing powder comprising egg and milk protein, the powder obtainable by creating a mixture of egg and milk protein,
pasteurizing the mixture at a temperature above 65°C,
drying the mixture.

4. The powder according to any of claim 1 to 3, wherein it is obtained without addition of stabilizing or emulsifying additives, and without adding water before pasteurization.

5. The powder according to any of claims 1 to 4, which is easily reconstitutable in water.

6. The powder according to any of claims 1 to 5, in which the milk proteins are a whey concentrate containing 35 to 80% by weight of proteins.

7. The powder according to any of claims 1 to 6, wherein the pasteurization temperature is above 67°C.

8. The powder according to any of claims 1 to 7, in which the egg is low temperature pasteurized whole egg.

9. The powder according to any of claims 1 to 8, in which at least 30% by weight of the dry matter content is derived from whey.

10. A food product or a beverage, which contains the powder according to any of claims 1 to 9.

11. A chilled dairy product, which contains pasteurized eggs as a texturizing agent and which has the same organoleptic properties of a product containing fresh eggs.

12. The product according to any of claims 10 to 11, which is free of other gelifying and texturizing agents, additives, hydrocolloids or gelatine.

13. A dairy product chosen from milk drinks, fromage frais, yoghurts and desserts, containing 0.5 to 10% by weight of the powder according to one of Claims 1 to 10.

14. The product according to any of claims 10 to 13, which is a gelled dessert of the flan type.

15. The product according to any of claims 10 to 13, which is a set or creamy fermented milk or yoghurt.

16. The product according to any of claims 10 to 13, which is an acid drink.

17. The product according to any of claims 10 to 13, which is a dessert mousse.

18. The product according to any of claims 10 to 13, which is a fromage frais.

19. The product according to claim 10, characterized in that it is a mayonnaise.

20. A process for preparing a powder according to any of claims 1 to 9, in which a concentrated lactic base rich in whey protein or in leguminous plant protein, and liquid egg is mixed, and then the mixture is pasteurized by heat treatment

at above 65°C while preserving the organoleptic and functional properties of the egg and it is dried.

21. Process according to claim 20, in which the egg component and the lactic base are mixed, the pH is adjusted, where appropriate, to a value ranging from 6.5 to 7.5, and the mixture is then pasteurized at a temperature of at most 78°C for 10-20 s.

22. Process for manufacturing the product according to any of claims 10 to 13 or 15, in which a mixture of whole milk or milk which has been skimmed to a greater or lesser degree, carbohydrates and the powder according to any of claim 1 to 9 is prepared by dissolution and the mixture is treated by lactic acid fermentation.

23. Use of the powder according to any of claims 1 to 9 as a replacement for egg in an egg-based food product.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/32 A23L1/187 A23J3/08 A23B5/035 A23C9/154

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 364 966 A (CHANG) 21 December 1982 (1982-12-21) column 2, line 62 -column 3, line 3 column 3, line 30 - line 35 column 5, line 66 -column 6, line 8 column 6, line 19 - line 21; claims 1,3,4,6,9,11 --- -/--	1-5,7-12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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(57) Abstract

Process for preparing microcapsules comprising a flavourant embedded in a matrix material comprising spraying an aqueous emulsion, suspension or solution of the flavourant and the matrix material under the supply of air having a temperature of 50-120 °C while simultaneously introducing a spraying agent, and subsequently treating the sprayed product in a fluidized bed at a temperature of 0-120 °C to form a free-flowing product.

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PROCESS FOR PREPARING MICROCAPSULES CONTAINING A FLAVOURANT EMBEDDED IN A MATRIX MATERIAL AND PRODUCTS PREPARED BY USING THE PROCESS

The present invention relates to a process for preparing microcapsules containing a flavourant embedded in a matrix material comprising spraying an aqueous emulsion, suspension or solution of the flavourant and the matrix material under the supply of air to form a free-flowing product.

Microcapsules containing a flavourant having fragrance and/or taste properties are used in a variety of products, such as foods and drinks, confectionery products, medical products, tooth paste, detergents, cosmetic and sanitary articles.

Irrespective of the area of use it is important that the microcapsules are stable by which is meant that the content of flavourant is maintained substantially unchanged. This implies that the flavourant must not escape or be converted, e.g. by reaction with the oxygen of the air or by reaction with other substances.

Herein flavourants mean substances having fragrance and/or taste properties. Flavourants are typically volatile compounds which tend to evaporate quickly unless they are encapsulated effectively in a non-reactive encapsulant.

Various processes for preparing microcapsules of the type mentioned above for use in chewing gum are known. When using such microcapsules in chewing gum the aim is to obtain a gradual release of the flavourant and control of the release so that the chewing gum maintains its flavour even when it is chewed for longer periods of time, such as several minutes.

US patent specification No. 4,386,106 discloses a process wherein the matrix material comprises gelatine, natural gum and a plasticizer and wherein an aqueous emulsion of a flavourant and the matrix material is roll dried to form a solid mass which is subsequently ground to form a powder, and the powder formed is coated with a water-insoluble material consisting of polyvinyl acetate, polyvinyl alcohol, zein or ethyl cellulose.

WO 89/05590 discloses a method of making a chewing gum containing wax embedded ingredients, including powdered flavourants to obtain a delayed release of the wax embedded ingredients which are incorporated in the chewing gum in comminuted particle form.

It is also well known to prepare a free-flowing powder containing a flavourant by spray drying and by using a matrix material consisting of gelatine or natural gum and a carbohydrate, such as saccharose, fructose and corn sirup.

However, a powder containing a flavourant and prepared by a conventional spray drying method does not provide sufficient protection of the flavourant to prevent part of the flavourant from escaping during the preparation and before use of the powder, or as composite flavourants are often used, such as e.g. orange oil, the more volatile component will escape and the composite flavourant will change character as a result thereof. The particles formed are porous and do not have a sufficiently high resistance against oxygen to prevent the oxygen of the air from reacting with the flavourant and converting parts of said flavourant into undesired compounds, see i.a. Taylor, A. H. (1983), Encapsulation systems and their applications in the flavour industry. Food Flav. Ingr. Proc. Pckg, Sep. 1983, pp. 48-52.

Surprisingly, it has now been found that the drawbacks of the prior art spray drying methods can be reduced or eliminated by the process according to the invention, which process is characterized in that the aqueous emulsion, suspension or solution of a flavourant and matrix material is sprayed under the supply of air having a temperature of 50 to 120°C while simultaneously introducing a spraying agent, and in that the sprayed product is subjected to an additional drying in a fluidized bed at a temperature between 0 and 120°C.

In conventional spray drying hot air having a temperature of 180-300° is typically supplied. When the liquid particles formed by the spraying meet the very hot air, a steam explosion occurs which results in that the matrix material in which the flavourant is enclosed becomes porous and permeable to flavourant and oxygen. The

product formed typically has a particle density of from 0.7 to 0.9 g/ml.

In the process of the invention comprising drying the liquid drops at a much lower temperature a considerably more dense matrix material is obtained, said matrix material having a particle density of from 1.0 to 1.5 g/ml, preferably from 1.1 to 1.4 g/ml, and as a result thereof it becomes substantially non-permeable to both the flavourant enclosed in the matrix material and to the oxygen contained in the ambient air.

A further advantage of the process according to the invention is that the solid particles formed by the spray drying are spherical as opposed to the particles formed by conventional spray drying which are irregular. As a result of the regular spherical shape the surface area is smaller which results in a reduced exudation of the flavourant from the microcapsules. Furthermore a smaller part of the flavourant will be deposited on the surface of the particles than by conventional spray drying.

Furthermore, it is possible to obtain larger particles with the process according to the invention and hence a reduced relationship between the surface area and the volume compared to the conventional spray drying, said reduced relationship contributing to reduce the evaporation. Thus, the process according to the invention allows the preparation of microcapsules having a size interval in the range of from 50-800 μm, whereas the particle size interval for particles prepared by the prior art processes ordinarily is considerably more narrow and typically varies in the range of from 10 to 100 μm.

Moreover, it has surprisingly been found that by using an emulsion which furthermore comprises wax it is possible to obtain a microencapsulated product containing a flavourant, said product exhibiting a considerably extended flavour release in confectionery products, such as chewing gum.

The flavourants used in the process according to the invention are water in-soluble in most uses and may contain functional groups, such as alcohols, ethers, aldehydes, acetales, ketones, esters and

lactones and comprise e.g. terpenes, heterocyclic compounds and mixtures thereof having molecular weights of from approx. 100 to approx. 300 and having a boiling point below 180°C, or the flavourants may be constituted by essential oils having a content of the low molecular compounds mentioned above, such as anise oil, pine needle oil, jasmin oil, camphorated oil, wintergreen oil, lavender oil, melissa oil, rosemary oil, eucalyptus oil, citrus oils and peppermint oil and spice oils and extracts of spice oils, such as extracts of parsley oil, lovage oil and dill oil.

Examples of water-soluble flavourants are acidulants, such as citric acid, tartaric acid, malic acid, orthophosphoric acid; sweeteners, such as glycyrrhizin and glycyrrhizinate, and bitter substances, such as coffein.

As matrix material in the process according to the invention colloids may be used, such as vegetable gum, e.g. gum arabic, and tragacanth gum, starch, including modified starch, dextrins, proteins, e.g. gelatine, including gelatine recovered from fish and other marine animals, succinylated gelatine, soya protein and caseinates. Furthermore the matrix material may include saccharides, such as saccharose, sugar alcohols and synthetic sweeteners and mixtures thereof. An example of a preferred matrix former is gelatine having a Bloom strength of from 0 to 300. The selection of matrix material depends on the flavourant used. For instance different types of gum arabic produce different permeability.

In order to obtain a slow release of flavourant from the microcapsules the matrix material according to a preferred embodiment may further contain wax, preferably relatively hard, water-insoluble wax having a low penetrometer resistance and a melting point which is lower than the boiling point of the flavourant. In an emulsion or suspension the following proportion is used : from 1-15% by weight of flavourant, from 20-35% by weight of colloid and from 1-8% by weight of wax, and the wax constitutes from 5 to 20% by weight of the finished microcapsules, preferably about 10% by weight.

The waxes used may be natural waxes (wax esters), such as carnauba

wax and candelila wax or synthetic waxes which are typically long-chained carbonhydrides, such as petroleum wax, paraffin wax, Hartwachs SP1044 supplied by Dansk Voksfabrik, synthetic waxes, polyethylene wax, polyethylene glycol and polyethylene oxide having a high molecular weight, etc. or stearin. It is preferred to use hard, microcrystalline waxes having a melting point of from approx. 40° to approx. 120°C, preferably from about 60° to 90°C.

Additives, such as emulsifiers, complexing agents, plasticizers and antioxidants may be used in the matrix materials mentioned above.

As spraying agent in the process according to the invention hydrophilic agents which furthermore act as contact drying agents may be used and which may constitute a relatively large part of the product (up to 30%), such as starch, modified starch, tricalcium phosphate, lactose, mannitol, ethyl cellulose, coagulated albumin and cured gelatine, or hydrophobic agents which constitute a relatively small part of the product (2-10%) may be used , such as casein, stearat-Ca and stearat-Na, hydrogenated castor oil, polyoxide, talc, vegetable wax, preferably carnauba wax and candelila wax, and paraffin wax, preferably a wax marketed under the name Hartwachs SP1044. The waxes are preferably microcrystalline. A minimum of 1 part by weight of spraying agent is used per part by weight emulsion, suspension or solution. The melting point of the spraying agent is preferably higher than 40°C, most preferable from 80°C-130°C.

In the preparation of a microencapsulated flavour product for use in confectionery products, such as chewing gum, where a flavour extension is desired it is preferred to use a spraying agent which is relatively hydrophobic and/or insoluble in water, such as casein, wax, paraffin (petroleum wax). As a result thereof the solvent effect of the saliva on the microcapsules is reduced.

Theoretically an emulsion, suspension or solution containing volatile flavourants will lose constituents which are highly volatile in connection with a spraying in a hydrophobic spraying agent. On the other hand more compact particles having a higher total content of flavourant can be obtained after drying is

completed.

In a preferred embodiment of the process according to the invention an emulsion of an oil containing a flavourant is sprayed under oxygen-free conditions in an aqueous colloid solution which optionally may contain water-soluble flavourants, the oils drops having a diameter of from 0.2 to 10 µm, preferably about 1 µm. By using an emulsion of an oil containing a flavourant as starting material it is possible to prepare products having a content of flavourant of from 0.1-40% by weight, preferably from 15-20% by weight. A proportion of from 1/99 to 2/3 parts by weight of flavourant per part by weight of matrix material is preferably used. In a particularly preferred process according to the invention an emulsion which furthermore comprises wax is used.

The emulsion is preferably heated to between 20 and 80°C, adjusted to a viscosity of from 80 - 250 cP and sprayed into fine drops (diameter about 0.1 - 1.2 mm) by means of e.g. a disc sprayer in a spraying tower where the emulsion, at the moment of spraying, meets air having a temperature of between 50 and 120°C. As a result thereof the outer part of the matrix material in the drops solidifies, thereby forming a shell so that the particles no longer are permeable to the flavourants but so that water is still allowed to diffuse. The formation of the shell may optionally be expedited further by blowing a spraying agent in the form of e.g. corn starch into the spraying tower. In case it is not desired that the spraying agent constitutes a greater amount in the shell formation, a spraying agent such as calcium stearate, a wax marketed under the name Hartwachs SP1044 or hydrogenated caster oil can be used.

In a further preferred embodiment of the process according to the invention an emulsion of an oil containing a flavourant and an aqueous colloid solution is sprayed under the supply of air having an temperature of 60 - 85°C and the sprayed product is subsequently subjected to a further treatment in a fluidized bed at a temperature of between 20 and 85°C.

The drying of the product in a fluidized bed is preferably effected with dehumidified air. The drying time is between 1 and 10 hours

depending on the bach size to obtain a product having a water content of from aprrox. 2 to approx. 7%.

Furthermore the invention relates to microcapsules comprising a flavourant embedded in a matrix material, the microcapsules being prepared by spraying an aqueous emulsion, suspension or solution of flavourants and the matrix material under the supply of air having a temperature of 50 to 120°C while simultaneously introducing a spraying agent, and the sprayed product is subsequently subjected to a further drying in a fluidized bed at a temperature of between 0 and 120°C.

Finally the invention relates to a chewing gum containing the microcapsules mentioned above.

Example 1

Microencapsulation of orange oil.

2000 g of Water was heated to 60°C, 2000 g of modified starch ("N-Lok®") was added and dissolved under stirring.

The solution was deaerated under vacuum at 0.8 bar at 65°C for 2 hours. Vacuum in the container was reduced by introducing nitrogen and subsequently the solution was cooled to 13°C, and 1000 g of orange oil was added slowly under vigoruos stirring. The orange oil was added by pressing out the orange oil from the raw material container using nitrogen at 0.1-0.5 bar.

The orange oil was emulsified in the N-Lok® solution within 1 hour. During the oil emulsification the viscosity was maintained at about 450 cP.

The emulsion container was heated to 40°C and the viscosity was adjusted to 112 cP by the addition of water which was deaerated for oxygen.

The emulsion was introduced into a spraying tower at a velocity of 2 l/min. and sprayed therein in the form of fine drops (about 0.1-0.3

mm) in a cloud of fine particles of spraying agent in the form of corn starch which was supplied simultaneously to the spraying tower from a hopper at a velocity of 4 kg/min. The spraying was effected by means of a disc sprayer having 2500 rotations/min.

The temperature in the spraying tower was 66°C and during the passage down through the tower the surface of the emulsion drops solidified. The retention time in the spraying tower was estimated to 1 - 2 sec.

The emulsion drops having freshly solidified surfaces were transferred to a fluidized bed and maintained fluidized for about 2.5 hours by the introduction of a drying air having a temperature of 65°C. During the drying the excess corn starch was recycled to the hopper.

The ready-dried product was subsequently removed and sieved into two fractions, viz. a product fraction of 53-300µm and a coarse fraction. The product fraction constituted 98% of the dried product.

The product obtained was a free-flowing product having a high particle density and a content of orange oil of 17.1%. The product is soluble in cold water and suitable as a flavourant in soft drinks.

Example 2

Microencapsulation of butter flavour

700 g of Water was heated to 60°C, 438 g of dextrine ("Moresweet 1924®") and 292 g of gum arabic were added and dissolved under stirring. In order to provide the solution with a butter-like look 24 g of a 1% solution of betacarotene in water was added. In another container 15 g of Viscoleo® extra (coconut oil containing C_{8-10} fatty acids) was mixed with 15 g of a liquid butter flavour, lot 15.94.251 supplied from International Flavors og Fragrances I.F.F. (Denmark) APS. In order to prevent oxidation a mixture of α-, β- and γ-tocopherol in an amount of 1% was added to the oil mixture.

The oil mixture was emulsified into the hot gum arabic/dextrin solution under nitrogen. The comminution of the oil drops was stopped at a size of 0.5-1 µm and the viscosity was adjusted to 120 cP at 60°C by dilution with water.

The emulsion was introduced into a spraying tower at a velocity of 1 l/min. and sprayed therein in the form of fine drops (about 0.3-0.8 mm) in a cloud of fine particles of the spraying agent which was supplied simultaneously to the tower from a hopper. The spraying agent was introduced at a velocity of 1.5 kg/min. The spraying was effected by means of a disc sprayer having 1200 rotations/min.

The temperature was 65°C in the spraying tower and during the passage down through the tower the surface of the fine drops solidified.

The emulsion drops having freshly solidified surfaces were transferred to a fluidized bed and maintained fluidized for about 1 hour by the introduction of drying air having a temperature of 65°C. During the drying the excess spraying agent was recycled to the hopper containing auxiliary agents.

The ready-dried product was removed and sieved into two fractions, viz. a product fraction of 250-820 µm and a coarse fraction of more than 820 µm.

The product obtained was a free-flowing product having a high particle density and a content of butter flavour of 1.5%. The product was dissolved in cold water at 10°C in less than 30 sec.

Example 3

Microencapsulation of eucalyptus oil

10 kg of Water was heated to 52°C, 4.446 kg of 240 Bloom type A gelatine and 2.223 kg of saccharose were added and dissolved in the water under stirring.

4.000 kg of eucalyptus oil having a content of 83% 1,8-cineol was

slowly emulsified into the gelatine/sugar solution under vigorous stirring. The comminution of the oil drops continued until the oil drops had a size of 1-2 µm.

The emulsion was subsequently heated to 70°C as the container was provided with a reflux condenser in order to avoid unneccesary loss of the eucalyptus oil at the high temperature. The viscosity was then adjusted to 180 cP by dilution with water.

The emulsion was now introduced into the spraying tower at a velocity of 2 l/min. and sprayed therein in the form of fine drops (about 0.2-0.3 mm) in a cloud of fine particles of spraying agent. The spraying agent was supplied to the spraying tower with a hot air stream of 85°C and in an amount of 3 kg/min. In order to ensure a rapid evaporation of water and to expedite the drying of the surface of the fine drops formed by spraying, additional air having a temperature of 85°C was supplied to the spraying tower in the spraying zone.

The spraying of the emulsion was effected by means of a disc sprayer having 2000 rotations/min. The temperature in the spraying tower was 65°C.

The emulsion drops having freshly solidified surfaces were transferred together with the spraying agent to a fluidized bed and maintained fluidized for about 2.5 hours by the introduction of drying air having a temperature of 63°C. During the drying the excess spraying agent was recycled to a hopper.

The ready-dried product was then removed and sieved into two fractions, viz. a product fraction of 53-300 µm and a coarse fraction. The product fraction constituted 97% of the dried product.

The product obtained was a free-flowing product having a high particle density and a content of eucalyptus oil of 17.7% and a content of 1,8-cineol of 14.62%. In other words a very insignificant loss of the most volatile component 1,8-cineol.

Example 4

Microencapsulation of mint oil

200 g of Water was heated to 60°C, 790 g of 240 Bloom type A gelatine was added and dissolved in water under stirring.

133.8 g of Carnauba wax was dissolved in 343 g of mint oil at 67-68°C to a homogeneous mixture.

The mint oil/wax mixture was slowly transferred to the gelatine/water solution under vigorous stirring. The comminution of the oil drops was continued until the oil drops had a size of 1 µm.

The viscosity was then adjusted to 180 cP by dilution with water.

The emulsion was now introduced into the spraying tower at a velocity of 3 l/min. and sprayed therein in the form of fine drops in a cloud of fine casein particles as spraying agent.

The spraying agent was supplied to the spraying tower with a hot air stream of 85°C and in an amount of 3-4 kg/min.

In order to ensure a rapid evaporation of water and to expedite the drying of the surface of the fine drops formed by spraying, additional air having a temperature of 85°C was supplied to the spraying tower in the spraying zone.

The spraying of the emulsion was effected by means of a disc sprayer having 2300 rotations/min. The temperature in the spraying tower was 65°C.

The emulsion drops having freshly solidified surfaces were transferred together with the spraying agent to a fluidized bed and maintained fluidized for about 3 hours by the introduction of drying air having a temperature of 63°C. During the drying the temperature of the encapsulated product did not exceed 40°C and the excess fine casein particles were recycled to a hopper.

The ready-dried product was then removed and sieved into two fractions, viz. a product fraction of 125-450 μm and a coarse fraction.

The product obtained was a free-flowing product having a high particle density of 1.2 g/ml.

The product is suitable for use in confectionery which requires an extension of flavour, e.g. chewing gum.

Example 5

Microencapsulation of spearmint oil

2000 g of Water was heated to 60°C, 790 g of 240 Bloom type A gelatine was added and dissolved in the water under stirring.

134 g of Carnauba wax was dissolved in 343 g of spearmint oil at 67°C.

The spearmint oil/wax mixture was slowly transferred to the gelatine/water solution under vigorous stirring. The comminution of the oil drops was continued until the oil drops had a size of 1 μm.

The viscosity was now adjusted to 160 cP by dilution with water.

The emulsion was then introduced into the spraying tower at a velocity of 3 l/min. and sprayed therein in the form of fine drops in a cloud of finely ground casein particles as spraying agent.

The spraying agent was supplied to the spraying tower with a hot air stream of 85°C and in an amount of 3-4 kg/min.

In order to ensure a rapid evaporation of water and to expedite the drying of the surface of the fine drops formed by spraying, additional air having a temperature of 85°C was supplied to the spraying tower in the spraying zone.

The spraying of the emulsion was effected by means of a disc sprayer

having 2300 rotations/min. The temperature in the spraying tower was 60°C.

The emulsion drops having freshly solidified surfaces were transferred together with the spraying agent to a fluidized bed and maintained fluidized for about 3 hours by the introduction of drying air having a temperature of 63°C. During the drying the temperature of the encapsulated product did not exceed 40°C and the excess finely ground casein particles were recycled to a hopper.

The ready-dried product was then removed and sieved into two fractions, viz. a product fraction of 125-450 µm and a coarse fraction.

The product obtained was a free-flowing product having a high particle density.

Example 6

Microencapsulation of orange oil

2000 g of Water was heated to 60°C, 790 g of 240 Bloom type A gelatine was added and dissolved in the water under stirring.

735 g of Lunacerin® W70 (paraffin wax) was melted at 73°C and 200 g of cold orange oil was added and the mixture was heated to 60°C.

The orange oil/wax mixture was slowly transferred to the gelatine/water solution under vigorous stirring. The comminution of the oil drops was continued until the oil drops had a size of 1 µm.

The viscosity was then adjusted to 160 cP by dilution with water.

The emulsion was then introduced into a spraying tower at a velocity of 3 l/min. and sprayed therein in the form of fine drops in a cloud of fine wax particles (Hartwachs SP1044 supplied from Dansk Voksfabrik) as spraying agent.

The spraying agent was supplied to the spraying tower with a hot air

stream of 85°C and in an amount of 3-4 kg/min.

In order to ensure a rapid evaporation of water and to expedite the drying of the surface of the fine drops formed by spraying, additional air having a temperature of 85°C was supplied to the spraying tower in the spraying zone.

The spraying of the emulsion was effected by means of a disc sprayer having 2300 rotations/min. The temperature in the spraying tower was 55°C.

The emulsion drops having freshly solidified surfaces were transferred together with the Hartwachs SP1044 spraying agent to a fluidized bed and maintained fluidized for about 3 hours by the introduction of drying air having a temperature of 63°C. During the drying the temperature of the encapsulated product did not exceed 40°C and the excess fine Hartwachs SP1044 particles were recycled to a hopper.

The ready-dried product was then removed and sieved into two fractions, viz. a product fraction of 125-450 µm and a coarse fraction.

The product obtained was a free-flowing product having a high particle density.

Example 7

Evaluation of encapsulation of flavourants

A taste panel consisting of 10 persons tasted 6 different pieces of chewing gum and reported the time within which the flavourant could be tasted after the point of start. Table 1 below shows the average values in seconds obtained for three different flavour products in chewing gum formulations comprising the flavour products in encapsulated and non-encapsulated form, respectively. In addition to 1-2% flavourant the chewing gum formulation further comprises about 20% sugar, about 24% gum base and about 56% paraffin.

Preparation of chewing gum containing flavour oil or coated flavour

24 g of Gum base was melted and 56 g of melted paraffin and 20 g of sugar were added under vigorous stirring. 1.4-10 g of Flavourant was added under stirring at 48-50°C. The flavourant was used in an amount corresponding to 1.4 g pure oil. In the addition of microencapsulated flavourant the amount added corresponds to about 1-2% by weight of the finished chewing gum.

Stirring was continued until solidification occured. The chewing gum which had started to solidify was poured out onto a glass plate and was pressed flat by another glass plate. The chewing gum was then allowed to stand for the night. The next day the chewing gum was cut into small pieces of 0.95-1.10 g.

Table 1

Flavourant	Initial taste in sec. after beginning of tasting	
Mintflavour	5	Not encapsulated
Encapsulated mintflavour	90	Encapsulated according to example 4
Spearmint flavour	2	Not encapsulated
Encapsulated spearmint flavour	25	Encapsulated according to example 5
Orange oil	1	Not encpasulated
Encapsulated orange oil	23	Encapsulated according to example 6

The results in table 1 show that by using flavourants which are encapsulated according to the invention in chewing gum a considerable extension of flavour start is obtained compared to chewing gum which contains non-encapsulated flavourants.

Example 8

Microencapsulation of extract of parsley oil

600 g of Water was heated to 35°C, 330 g of fish gelatine and 330 g of saccharose were added and dissolved under stirring.

50 g of Extract of parsley oil was emulsified into the fish gelatine/saccharose mixture. The comminution of the oil resulted in an average oil drop size of 0.7 µm.

The viscosity was adjusted to 112 cP at 35°C by dilution with water.

The emulsion was introduced into a spraying tower at a velocity of 1.5 l/min. and sprayed therein in the form of fine drops in a cloud of fine particles of corn starch which was supplied simultaneously time to the tower from a hopper. The spraying agent was introduced into the spraying tower at a velocity of 1.5 kg/min. The spraying was effected by a disc sprayer having 1200 rotations/min. The temperature in the spraying tower was 68°C and during the passage down through the tower the surface of the fine drops formed by spraying solidified.

The emulsion drops having freshly solidified surfaces were transferred to a fluidized bed and maintained fluidized for about 8 hours at a temperature of 30°C. During the drying the excess corn starch was recycled to the hopper.

The ready-dried product was removed and sieved into two fractions, viz. a product fraction of 100-500 µm and a coarse fraction of more than 500 µm.

A water vapour distillation according to the Clevenger Method showed a parsley oil content of 5.2%.

Example 9

Microencapsulation of extract of lovage oil

600 g of Water was heated to 40°C, 330 g of fish gelatine and 330 g of saccharose were added and dissolved under stirring.

50 g of Extract of lovage oil was emulsified into the fish gelatine/saccharose mixture. The viscosity was adjusted to 116 cP at 40°C by dilution with water.

The emulsion was introduced into a spraying tower at a velocity of 1.5 l/min. and sprayed therein in the form of fine drops in a cloud of fine particles of corn starch which was supplied simultaneously to the tower from a hopper. The spraying agent was introduced into the spraying tower at a velocity of 1.5 kg/min. The spraying was effected by a disc sprayer having 1200 rotations/min.

The temperature in the spraying tower was 65°C and during the passage down through the tower the surface of the fine drops formed by spraying solidified.

The emulsion drops having freshly solidified surfaces were transferred to a fluidized bed and maintained fluidized for about 8 hours a temperature of 30°C. During the drying the excess corn starch was recycled to the hopper. The ready-dried product was removed and sieved into two fractions, viz. a product fraction of 100-500 µm and a coarse fraction of more than 500 µm.

A water vapour distillation according to the Clevenger Method showed a lovage oil content of 6.3%.

Example 10

Microencapsulation of extract of dill oil

3000 g of Water was heated to 65°C, 1994 g of 0-10 Bloom gelatine and 1994 g of saccharose were added and dissolved under stirring. The solution was deaerated under vacuum at 0.81 bar for 2 hours at

65°C. The vacuum in the container was decreased by introduction of nitrogen and 900 g of extract of dill oil added with 1.28 g of mixtocopherol was emulsified into the gelatine/saccharose mixture to an oil drop size of 1 µm.

The viscosity was then adjusted to 80 cP at 62°C by the addition of water which was deaerated for oxygen.

The emulsion was introduced into a spraying tower at a velocity of 1.5 l/min. and sprayed therein in the form of fine drops (about 1.1-0.3 mm) in a cloud of fine particles of spraying agent in the form of corn starch which was supplied simultaneously to the tower at a velocity of 2 kg/min. The spraying was effected by a disc sprayer having 2000 rotations/min.

The temperature in the spraying tower was 65°C and during the passage down through the tower the surfaces of the emulsion drops solidified.

The emulsion drops having freshly solidified surfaces were transferred to a fluidized bed and maintained fluidized for about 3 hours at a temperature of 40°C.

During the drying the excess corn starch was recycled to the hopper.

The ready-dried product was then removed and sieved into two fractions, viz. a product fraction of 100-500 µm and a coarse fraction of more than 500 µm.

A water vapour distillation according to the Clevenger Method showed a content of extract of dill oil of 14.7%. An analysis by means of HPLC (high performance liquid chromatography) showed a content of extract of dill oil of 15.1%.

Example 11

750 g of Water was heated to 65°C, 312 g of 240 Bloom type A gelatine and 115 g of glycyrrhizin having a concentration of 90.7% glycyrrhizin were added and dissolved under stirring.

The viscosity was adjusted to 160 cP at 65°C by dilution with water.

The solution was introduced into the spraying tower at a velocity of 1.5 l/min. and sprayed therein in the form of fine drops in a cloud of fine carnauba wax particles (carpol 1305) which were supplied at the same time to the tower from a hopper.

The spraying agent was introduced into the tower at a velocity of about 2 kg/min. The spraying was effected by a disc sprayer having a velocity of 1200 rotations/min and the temperature in the spraying tower was 65°C.

The emulsion drops having freshly solidified surfaces were transferred together with the carnauba wax spraying agent to a fluidized bed and maintained fluidized for about 3 hours by the introduction of a drying air having a temperature of 38°C.

The excess fine carnauba wax powder was recycled to the hopper. The ready-dried product was then removed and sieved into two fractions, viz. a coarse fraction and a product fraction of 125-420 μm.

The product can be used as a flavourant in confectionery.

Patent Claims

1. A process for preparing microcapsules containing a flavourant embedded in a matrix material comprising spraying an aqueous emulsion, suspension or solution of the flavourant and the matrix material under the supply of air to form a free-flowing product, characterized in that the spraying is effected under the supply of air having a temperature of 50 to 120°C while simultaneously introducing a spraying agent, and in that the sprayed product is subjected to a further drying in a fluidized bed at a temperature between 0 and 120°C.

2. A process according to claim 1, characterized in that an emulsion of an oil containing a flavourant and aqueous colloid solution is sprayed under the supply of air having a temperature of from 60° to 85°C, and that the sprayed product is subjected to an additional treatment in a fluidized bed at a temperature between 20 and 85°C.

3. A process according to claims 1 or 2, characterized in spraying an emulsion comprising oil drops containing a flavourant having a diameter of from 0.2-10 μm.

4. A process according to any of the preceding claims, characterized in using a colloid, such as gum arabic, modified starch, glucose sirup, dextrines and gelatine or mixtures thereof as matrix material.

5. A process according to claim 4, characterized in using gelatine having a Bloom strength of from 0-300, preferably from 30-300, as matrix material.

6. A process according to any of the preceding claims, characterized in that the matrix material further comprises wax.

7. A process according to claim 6, characterized in that the wax is carnauba wax, candelila wax, paraffin wax, a wax marketed under the name Hartwachs SP1044 and synthetic waxes.

8. A process according to any of the preceding claims, c h a r a c t e r i z e d in using as spraying agent modified starch, casein, tricalcium phosphate, lactose, ethyl cellulose, coagulated albumin, stearic acid, cured gelatine, calciumstearat and sodiumstearat, hydrogenated castor oil, polyoxide, talc, vegetable wax and paraffin wax or mixtures thereof in a proportion of at least 1 part by weight of spraying agent per part by weight of emulsion, suspension or solution.

9. A process according to any of the preceding claims, c h a r a c t e r i z e d in using a proportion of from 1/99 to 2/3 parts by weight of flavourant per part by weight of matrix material.

10. A process according to any of the preceding claims, c h a r a c t e r i z e d in using from 1-15% by weight of flavourant, from 20-35% by weight of colloid and from 1-8% by weight of wax in the emulsion or suspension.

11. Microcapsules comprising a flavourant embedded in a matrix material, c h a r a c t e r i z e d in that the microcapsules are prepared by spraying an aqueous emulsion, suspension or solution of flavourants and the matrix material under the supply of air having a temperature of from 50 to 120°C while simultaneously introducing a spraying agent, and that the sprayed product is subjected to an additional drying in a fluidized bed at a temperature between 0 and 120°C.

12. Microcapsules prepared according to claims 6, 7 or 8, c h a r a c t e r i z e d in that wax constitutes from 5-20% by weight of the microcapsule.

13. Microcapsules according to claims 11 or 12, c h a r a c t e r i z e d in that the flavourant constitutes from 0.1 - 40% by weight of the finished microcapsules.

14. Microcapsules according to claims 11, 12 or 13, c h a r a c t e r i z e d in that the finished microcapsule has a particle size of from 50 to 1000 µm.

15. Microcapsules according to claims 11, 12, 13 or 14, c h a r a c t e r i z e d in that the particle density varies within the range of 1.0-1.5 g/ml.

16. A chewing gum containing microcapsules comprising a flavourant embedded in a matrix material, c h a r a c t e r i z e d in that it contains microcapsules according to claim 11.

17. A chewing gum containing microcapsules comprising a flavourant embedded in a matrix material, c h a r a c t e r i z e d in that it contains microcapsules according to claim 12.

INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 91/00133

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: B 01 J 13/04, A 23 G 3/30

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	B 01 J; A 23 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP, A1, 0070719 (UNILEVER PLC ET AL) 26 January 1983, see page 5, line 27 - page 7, line 29; page 9, line 5 - page 10, line 2 --	1-5,8-11,13-15
A	US, A, 4695463 (YANG ET AL) 22 September 1987, see column 5, line 32 - line 40; column 6, line 38 - column 8, line 17; column 11, line 35 - column 12, line 37 --	1-17
X	US, A, 4519961 (SCHUMACHER ET AL) 28 May 1985, see column 2, line 42 - line 49; column 4, line 26 - line 49; claim 6 --	1-5,8-11,13-15

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22nd August 1991	1991 -08- 27
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Eva Iversen Hasselrot

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4122195 (BAHOSHY ET AL) 24 October 1978, see the whole document --	1-17

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/DK 91/00133

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 91-06-27 The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		AU-D-	8612182	83-01-27
		CA-A-	1190477	85-07-16
		JP-C-	1584973	90-10-31
		JP-B-	2001528	90-01-11
		JP-A-	58024336	83-02-14
		US-A-	4576737	86-03-18
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		US-A-	4139639	79-02-13

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(57) Abstract

The invention relates to a process for preparing a particulate, flowable, glucose product comprising spray drying glucose syrup together with recycled dry powdered glucose to form a particulate material, wherein said particulate material is passed into a first retention zone for a first crystallisation period, then into a drying zone and subsquently into a second retention zone for a second evaporation and crystallisation period, the resulting product being milled and sifted to produce a final glucose product together with dry powdered glucose which is recycled to be spray dried. Such a process results inthe production of a high quality, free-flowing, dried glucose product of uniform consistency.

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Spray Drying

The present invention relates to a process for the preparation of a dried glucose product from glucose syrup and in particular to the preparation of such a product having an improved, uniform consistency.

Such syrup produced by the hydrolysis of various starches has been a valuable material for use in the food industry for many years. However, whilst glucose in liquid form is suitable for many applications eg. confectionery, brewing and baking, there are certain areas of the food industry in which glucose in a solid form is desirable eg. dry mixes, etc.

There are two conventional methods for obtaining glucose in a solid form from glucose syrups: slow crystallisation of pure glucose from the syrup leaving a residual mother liquor containing various impurities, and solidification of a mixture of glucose, higher sugars and impurities as a "total sugar". The first of these methods is relatively expensive in terms of capital outlay for equipment. Furthermore, it is slow in operation and a relatively large part of the glucose remains in the mother liquor which can only be sold at a low price. In addition, the final glucose product has a degree of purity well beyond that required for the food industry where the glucose product is mixed with other raw materials during use.

In view of the better economics of the second method, a number of attempts have in the past been made to realise such a method on an industrial scale. However, normal spray drying has not proved practicable due to the slow rate of crystallisation of the glucose which results in a sticky mass formed on the walls of the spray drier, and resultant downstream handling problems.

The basic spray drying procedure has been modified

by utilization of a seeded spraying technique in which syrup is sprayed over a recycled portion of the spray dried powder. The spray droplets mix with falling particles of recycled powder before falling to the bottom of the spray drier and onto the moving belt in a controlled manner. From the end of the belt the product is passed to a rotating drum and following sieving and grinding, a reasonably free flowing powder is produced, part of which may be recycled into the spraying process.

There is however the need for an improved process for the preparation of a flowable dried glucose product which is of a desired, consistent, particle size for use as a food product.

Thus, viewed from one aspect the present invention provides a process for preparing a crystalline, flowable, glucose product comprising spray drying glucose syrup together with recycled dry powdered glucose to form a particulate material, wherein said particulate material is passed into a first drying zone for a first evaporation and crystallisation period, then into a further drying zone and subsequently into a separate retention zone for a further evaporation and crystallisation period, the resulting product being milled and sifted to produce a final glucose product together with dry powdered glucose which is recycled to be spray dried.

The glucose syrup used in the process of the invention is preferably maize-derived with a glucose content (on a dry solids basis = DS) of 75 to 80% by weight and a high dextrose equivalent of between 95 and 99.

Maize-derived syrup gives rise to a product having different color, flow and fragrance than a non demineralised wheat-derived glucose.

The recycled dry powdered glucose used in the process of the invention preferably has a water content not exceeding 8% by weight and a glucose content of 94%

DSB. In normal operation it will comprise recycled particles from the milling and sifting operation subsequent to second stage retention. For process start up however any glucose powder of reasonable dryness (≤10% water content) and purity (≥90% glucose DS) may be used.

The first stage of the process involves the use of a spray drier, such as the Filtermat spray drier (from Niro A/S of Denmark) in which the moisture of the product is preferably reduced from 20-25% to 2-8% in order to provide a semi-crystalline product. In the spray drier, glucose syrup is spray dried together with recycled dry powdered glucose, e.g. in a solids weight ratio of about 2-4 to 1, preferably onto a moving surface such as a belt which then passes into a first retention zone for a short crystallisation period of, for example, 5 to 8 minutes, at 45 to 75°C. It is during this first retention period that water becomes bound into the semi-crystalline structure of the glucose product.

The sprayed product, conveniently still on the belt, then moves through a secondary drying zone which ensures the removal of any remaining free moisture from the glucose product. The product remains in this zone for 12 to 15 mins, preferably at a temperature of 45 to 60°C. Following this secondary drying process, substantially only the bound water molecules remain.

The temperature within the spray drier needs to be carefully controlled and should preferably be maintained at a temperature above the optimum temperature for crystal formation. Preferably the inlet temperature for the air in the spray drier is about 130°C and the outlet temperature is about 60-70°C, with the inlet temperature of the glucose syrup being about 70°C.

The product from the spray drier is then conveyed into a second retention zone to allow further evaporation and crystallisation to occur. Suitable

retention equipment includes a rotating drum in which the product is preferably held for a period of 15 mins to 1 hour at a temperature of 60°C.

The product discharged from the second retention zone will typically be of a particle size in the range of from 1 to 3 mm and must therefore be further milled and sifted to produce a particle size required for both the final product and for recycling to the spray drier. Such selection of an optimum particle size of 80% < 200 μm for recycling results in the production of a high quality, free-flowing dried glucose product of uniform consistency. The moisture content of the final product is preferably in the range of from 1 to 2% by weight.

The process of the invention may be carried out using conventional spraying equipment. However, in order to ensure the required final product quality, such equipment must comprise suitable retention apparatus for complete crystallisation of the product and suitable product sizing apparatus to ensure the correct size reduction of the product to form the necessary quality of recycled product.

Viewed from a further aspect the invention also provides a spray drying apparatus for performing the process of the invention, comprising means for spray drying glucose together with recycled dry powdered glucose, a rotating drum to assist crystallisation of the spray dried product, means for milling and sifting the resulting product to produce a final glucose product together with dry powdered glucose, and means for recycling the dry powdered glucose to be spray dried.

The apparatus for performing the process of the invention preferably further comprises a de-lumper located upstream of the second retention zone. Such equipment ensures that any large slabs of product emerging from the spray drier are broken up into smaller pieces prior to entering the second retention zone. In this way, the de-lumper helps to ensure the production

of particles of the size required for both the final product and for recycling to the spray drier. The de-lumper conveniently comprises a 4-bladed rotor sited within a uniformly perforated metal screen.

The means for recycling the dry powdered glucose to the spray drier conveniently comprises a conduit, eg. a conventional pipe, through which the dried glucose product travels under pneumatic pressure. Such a conduit may split into two or more, preferably about 10, sub-conduits each of which carries the recycled powder to separate high pressure nozzles located in the upper part of the spray drying chamber. The conduit conveniently splits at a point near to the top of the spray drying chamber. It has however been found that a better flow of recycled product is achieved if the conduit splits after turbulent flow in the conduit has ceased.

The process of the present invention results in the formation of a dried glucose product having superior physicochemical characteristics to those products produced by conventional spray drying techniques. In particular, the process of the invention inherently results in the formation of an amorphous product having a particularly low moisture content and a high initial water solubility at ambient temperature.

Viewed from another aspect, the invention thus provides a spray dried glucose product having an amorphous structure, a moisture content of less than 1% by weight and a solubility in water at ambient temperature of at least 55% by weight.

By "amorphous" it is meant that the spray dried product has a porous, sponge-like, high surface area structure with a degree of crystallinity $\leq$ 99% by weight.

Preferably, the spray dried product of the invention has a degree of crystallinity in the range of from 80 to 96%, more preferably 87 to 90%.

The crystallinity values referred to herein are measured by Differential Scanning Calorimetry (DSC) relative to absolute as determined by anhydrous dextrose which has a degree of crystallinity of 100% by weight.

The solubility of the spray dried product of the invention, at ambient temperature, is preferably in the range of from 55 to 63% by weight, more preferably 60 to 63%, especially 62-63%. The values given for solubility are the number of grams which dissolve in 100 grams of solution at ambient temperature. For example, 60% = 60g of product in 100g of solution.

The drying conditions used in the process of the invention moreover result in the formation of a glucose product comprising a large proportion of glucose in the β-form. Typically, the spray dried glucose product may contain up to 60% by weight of β-glucose.

The physical characteristics of the spray dried particles produced in accordance with the invention enable them to be readily compressed to form eg. tablets without the need for any further treatment and/or addition of low levels of a lubricant. For example, it has been found that both fine and coarse grades of the particles flow particularly readily into the dies of various tabletting machines, enabling the production of hard tablets of consistent weight up to speeds of 7000 tablets per minute.

The glucose product of the invention is thus of particular use in the food industry, especially in confectionery eg. in the production of hard centred sweets.

The glucose product of the invention is also of particular use in the pharmaceutical industry due to its tabletting properties which enable the ready preparation of tablet cores.

Preferred embodiments of the invention will now be described by way of example and with reference to the accompanying figures, in which:

Figure 1 schematically illustrates apparatus which represents an embodiment of the invention;

Figure 2 schematically illustrates apparatus which has a de-lumper and which represents a further embodiment of the invention;

Figures 3 and 4 are electronmicrographs (Magnification x 450 and x 4000 respectively) of spray agglomerates produced in accordance with the process of the invention;

Figure 5 is an electronmicrograph (Magnification x 300) of a spray dried dextrose monohydrate product produced by a conventional process.

Referring to Figure 1, in normal operation, glucose syrup and recycled dry powdered glucose enter the spray drying chamber 1 via inlet means 2 and 3 respectively. The feed pressure in each nozzle 19 is conveniently in the range of from 80 to 400 bar (60-90°C). A stream of hot drying air for use in the spray drying process, eg at a temperature in the range of from 140 to 175°C, enters the drying chamber 1 via inlet 4. The ratio by weight of feed material to recycled material entering the drying chamber is preferably between 2 to 4:1.

Drying air leaves the drying chamber 1 through multiple ducts 5 and any powder particles are separated from the air in cyclones 6. The drying air leaves the apparatus through a stack 15.

The spray dried product is collected as a porous cake on moving belt 7 which passes through a first retention zone 8 and subsequently through a secondary drying zone 9. The dried product then passes through a cooling zone 16 prior to being conveyed into rotating drum 10 for further evaporation and crystallisation. Drum 10 is preferably provided with hot air at an inlet temperature in the range of from 80 to 120°C. The air exits the drum at a temperature of from 50 to 90°C and is filtered and exhausted to the atmosphere. The resulting product leaves the drum with a moisture

content of from 0.5 to 1.0% by weight and is then pneumatically conveyed to a holding bin 20.

The resulting product is then passed through sifter 11 followed by grinder 12 to produce particles of a size required for both the final product 13 and for recycling to the spray drying chamber 1. Fine grade product passes into bin 17 and coarse grade product into bin 18. Each product is then bagged.

The particles for recycling are passed back to the spray drying chamber via pipe 14.

Figure 2 illustrates a preferred embodiment of the invention in which the dried product is passed through a de-lumper 21 prior to entering rotating drum 10. A second de-lumper may also be provided downstream of the sifter 11.

Figures 3 to 5 attached hereto illustrate the amorphous nature of the glucose product of the invention compared to the crystalline structure of dextrose monohydrate prepared by a conventional spray drying process. Table 1 below compares the product of the invention with dextrose monohydrate and sucrose.

Table 1

	Glucose product of the invention	Dextrose	Sucrose
Chemical Analysis (% by weight)	94% dextrose 3% maltose 3% higher sugars	>99.5% dextrose	>99.9% sucrose
Crystallinity measured by DSC = Differential Scanning Calorimetry (% by weight)	87-96%	100%	100%
Forms of α/β dextrose measured by polarimetry (% by weight)	60% β	100% α	*
Moisture content (% by weight)	<1%	8-9% <2% (anhydrous)	<0.02%
Maximum solubility in water at ambient temperature (% by weight)	62-63%	55%	67-68%

* Sucrose is a disaccharide and is thus not comparable

Claims:

1. A process for preparing a particulate, flowable, glucose product comprising spray drying glucose syrup together with recycled dry powdered glucose to form a particulate material, wherein said particulate material is passed into a first retention zone for a first crystallisation period, then into a drying zone and subsequently into a second retention zone for a second evaporation and crystallisation period, the resulting product being milled and sifted to produce a final glucose product together with dry powdered glucose which is recycled to be spray dried.

2. A process as claimed in claim 1 wherein said glucose syrup is maize-derived with a glucose content (DS) of 75 to 80% by weight and a dextrose equivalent of between 95 and 99.

3. A process as claimed in claim 1 or claim 2 wherein said particulate material has a water content of between 1 and 2% by weight.

4. A process as claimed in any one of claims 1 to 3 wherein said first crystallisation period is in the range of from 5 to 8 minutes.

5. A process as claimed in any preceding claim wherein said second retention zone comprises a rotating drum.

6. A process as claimed in any preceding claim wherein said second crystallisation period is in the range of from 15 minutes to 1 hour.

7. A glucose product produced by a process as claimed in any preceding claim.

8. Apparatus for performing a process as claimed in any one of claims 1 to 6 comprising means for spray drying glucose together with recycled dry powdered glucose, a rotating drum to assist crystallisation of the spray dried product, means for milling and sifting the resulting product to produce a final glucose product together with dry powdered glucose, and means for recycling the dry powdered glucose to be spray dried.

9. Apparatus as claimed in claim 8 further comprising a de-lumper located upstream of the rotating drum.

10. Apparatus as claimed in claim 8 or claim 9 wherein said means for recycling the dry powdered glucose comprises a conduit which splits into a plurality of sub-conduits each of which carries the powdered glucose into the means for spray drying.

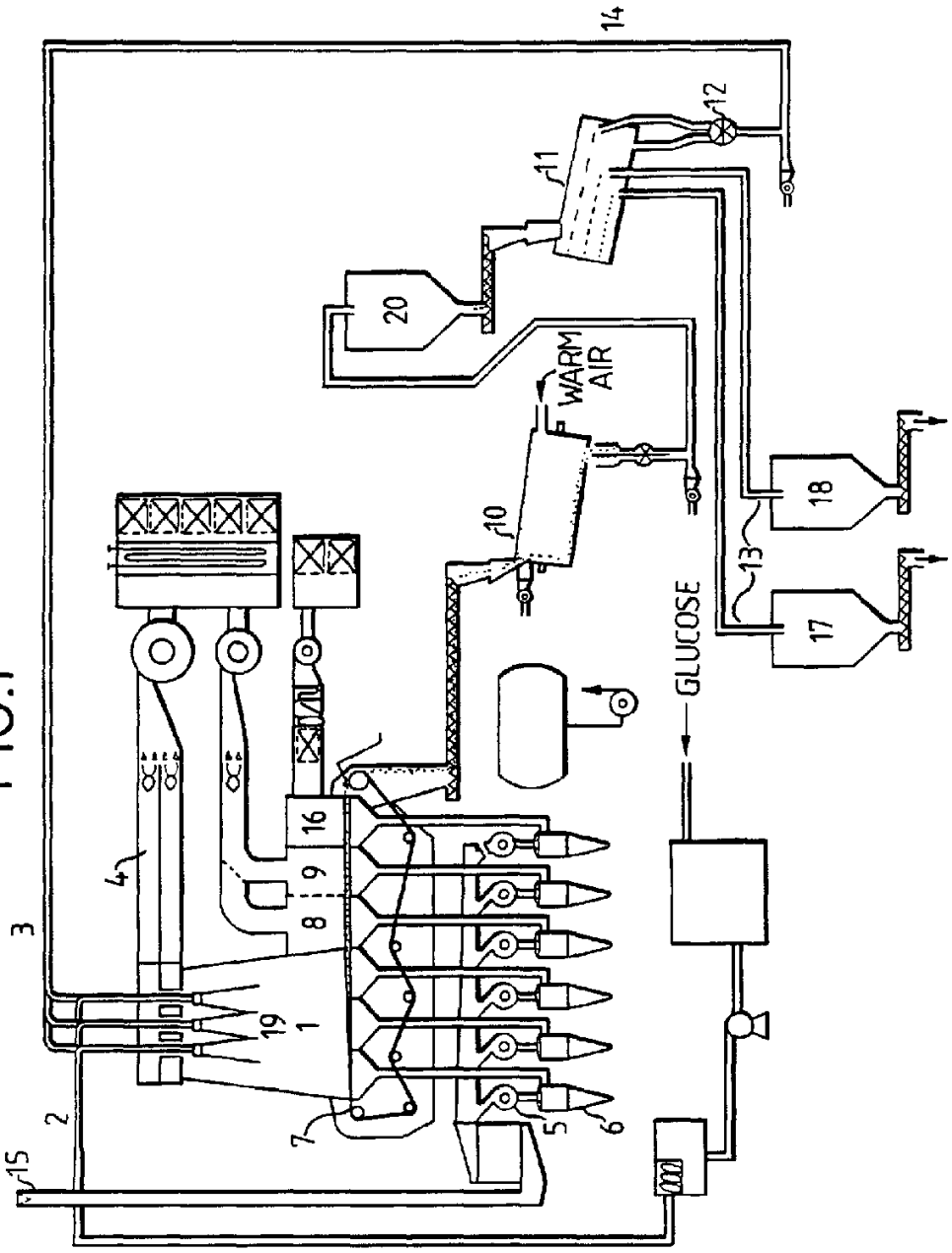
11. Apparatus as claimed in claim 10 wherein said conduit splits after turbulent flow has ceased.

12. A spray dried glucose product having an amorphous structure, a moisture content of less than 1% by weight and a solubility in water at ambient temperature of at least 55% by weight.

13. The use of a glucose product as defined in claim 12 in the production of compressed products.

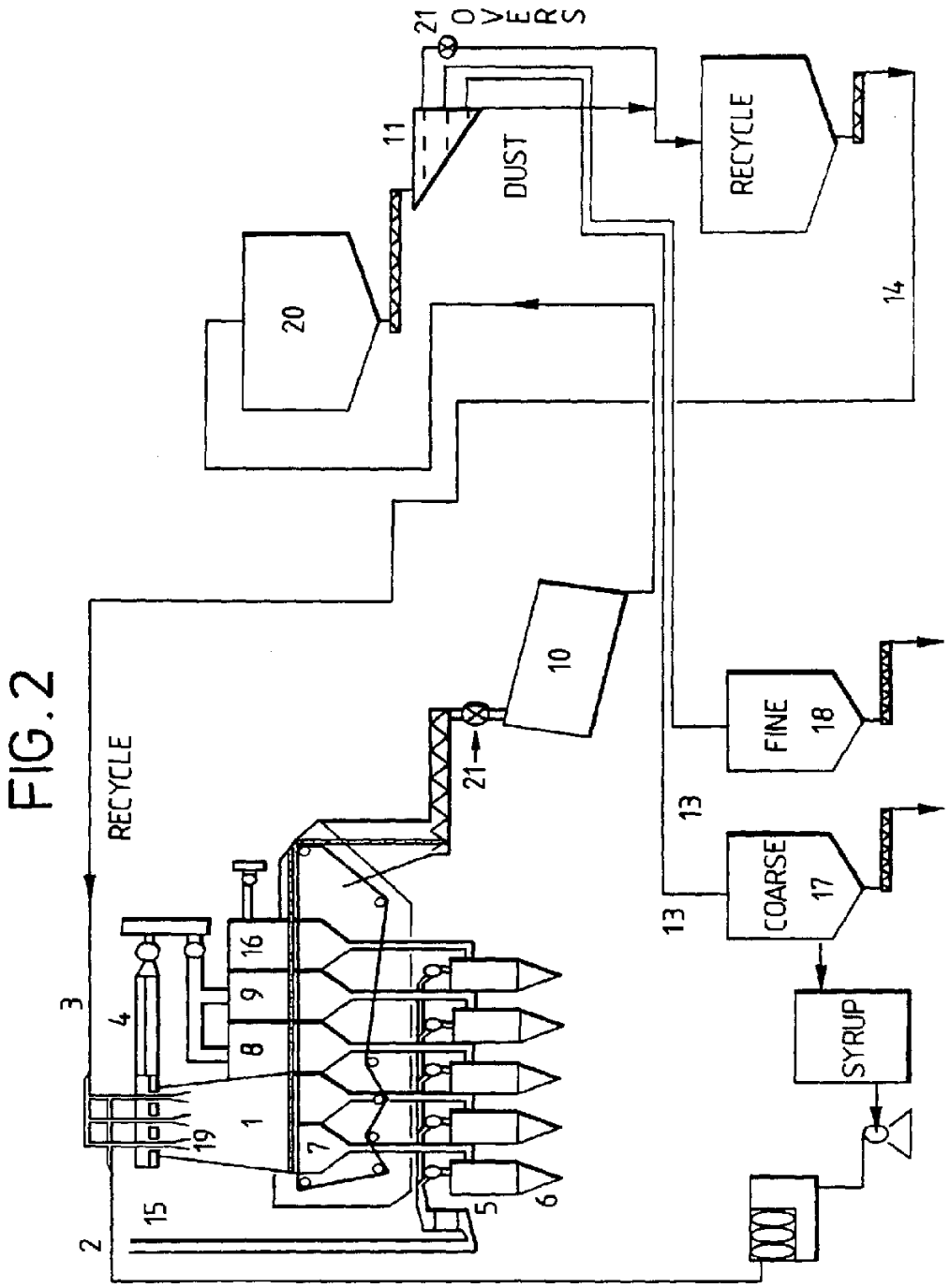
14. Use as claimed in claim 13 in the production of pharmaceuticals or confectionery.

FIG.1



IFF000658599

FIG. 2



IFF000658600

FIG. 3



FIG. 4



FIG. 5



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(54) Title: SPRAY DRYING

(57) Abstract

The invention relates to a process for preparing a particulate, flowable, glucose product comprising spray drying glucose syrup together with recycled dry powdered glucose to form a particulate material, wherein said particulate material is passed into a first retention zone for a first crystallisation period, then into a drying zone and subsquently into a second retention zone for a second evaporation and crystallisation period, the resulting product being milled and sifted to produce a final glucose product together with dry powdered glucose which is recycled to be spray dried. Such a process results inthe production of a high quality, free-flowing, dried glucose product of uniform consistency.

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BE,A,441 172 (GLUCOSERIES REUNIES) 31 May 1941 see claims; figure see page 2, line 18-33 see page 3, line 10-14 see page 4, line 13-16	1-3,7,8, 12-14
A	GB,A,2 132 495 (CPC INTERNATIONAL) 11 July 1984 see the whole document	1-14

☐ Further documents are listed in the continuation of box C.

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BE-A-441172		NONE	
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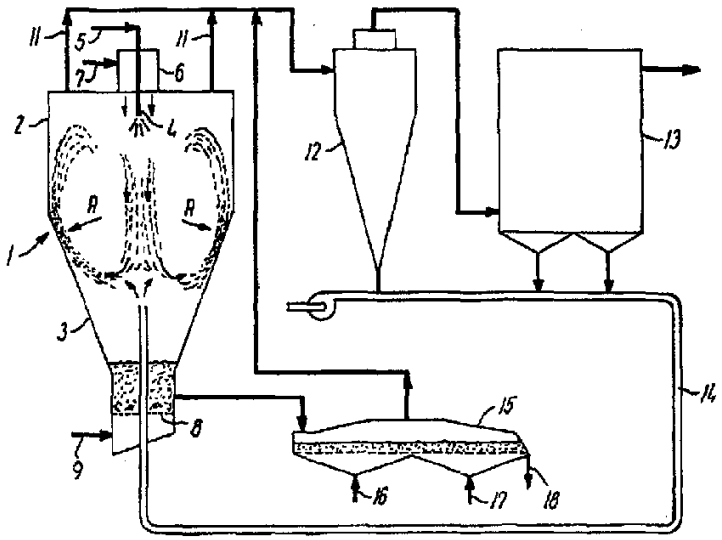
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(54) Title: A PROCESS AND A SPRAY DRYING APPARATUS FOR PRODUCING AN AGGLOMERATED POWDER



(57) Abstract

In a spray drying and agglomerating process carried out in a spray drying chamber (1) having a conical lower section (3), in which chamber the liquid to be spray dried is atomized into a downward central stream of drying gas and the spent drying gas is withdrawn from non-central locations (5, 11) in the upper part of the drying chamber together with entrained fine particles, the fine particles are recycled to the drying chamber by pneumatic injection thereof from a location in the lower part of the drying chamber and in one or more directions forming an angle of 0-90° to the upward center axis of the chamber. An apparatus suitable for carrying out the process has means for performing the separation and recycling of the fine particles as specified.

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A PROCESS AND A SPRAY DRYING APPARATUS FOR PRODUCING AN AGGLOMERATED POWDER.

Field of the Invention.

The present invention relates to a spray drying process and apparatus for the production of an agglomerated powder of solids from a liquid solution and/or dispersion thereof.

Background of the Invention and Prior Art.

In the spray drying of products which at certain combinations of temperatures and moisture contents are sticky, various processes and apparatuses are used to obtain the product as an agglomerated powder.

In certain of the spray drying systems used for this purpose the atomization of the liquid to be dried and at least a substantial part of the drying of the atomized liquid take place in a chamber of which the lower part is formed by a conical downward tapering section, and the liquid is atomized into a central downward stream of drying gas, whereas the spent drying gas is recovered together with entrained fine powder particles from non-central locations in the uppermost part of the chamber.

In the present specification the term "central" indicates locations on or near the vertical centeraxis of the chamber, whereas the term "non-central location" means any place between the central one and the periphery of the chamber. The above mentioned recovering of spent drying gas may thus for instance take place through an annular orifice surrounding the central downward stream of drying gas.

The product comprising agglomerated powder particles of suitable size is recovered from the bottom part of the conical section of the drying chamber.

The fine particles entrained with the spent drying gas and often forming a substantial part of the particles produced in the spray drying process are recovered by means of cyclones, bag filters or other conventional dust-separ-

ating equipment.

Since said fine particles will often be too small to fulfil the specifications set for the final product they are recycled to the chamber to contact wet droplets or sticky moist particles to form agglomerates of suitable size.

Said recycling are conventionally made to locations in the upper part of the spraying chamber, for instance in adjustable distance from the atomizing device, as disclosed in European patent application No. 378 498, alternatively the fine particles are injected tangentially along the chamber walls in the lower part of the chamber. It has also been suggested to inject the fine particles in an upward direction just below the atomizer device to have the fine particles intersect the part of the droplets ejected from the atomizer device, confer US patents Nos. 3 324 567, 3 460 600 and 4 279 873. However, this last mentioned system for recycling of the fine particles has been suggested only in connection with spray driers having a flow pattern substantially different from the one existing in the above described drying chambers in which the drying air is introduced in a central downward stream and leaves the chamber from non-central exits in the top of the chamber.

Among the spray drying processes of special interest in connection with the present invention are those, in which a layer of fluidized particles is maintained in the bottom of the spray drying chamber. Said fluidized layer receives partly dried particles formed by partial drying of droplets atomized in the upper part of the chamber. In the fluidized layer these spray dried particles are agglomerated and further dried either to the final moisture content or to a moisture content above the desired moisture content in the final product, but sufficiently low to enable recovering of the agglomerated powder for subsequent drying, for instance in a vibrated fluidized bed apparatus outside the drying chamber. A process of this type is described for example in European patent specification No. 97 484 and the

corresponding the US patent specification No. 4 490 403, incorporated herein by reference.

In the prior art systems having a fluidized layer in the bottom of the spray drying chamber, the fine particles separated from the spent drying gas are usually recycled directly to the fluidized layer for further agglomeration therein.

The present invention provides improvements in spray drying and agglomeration processes utilizing the typical flow pattern formed in a spray drying chamber, in which the centrally downward introduced drying air is withdrawn from non-central locations in the top of the spray drying chamber.

Such recovering of the spent drying gas from non-central locations in the top of the drying chamber is mainly, but not solely utilized in connection with systems having a fluidized layer in the bottom of the chamber, for which reason an essential feature of the invention is improvement of such processes and apparatuses utilizing an integrated fluid bed.

It is an object of the invention to improve the product quality of processes of the above described type to obtain desired large agglomerated particles having a low content of dustforming small particles and having a very low degree of heat damage.

An other object is to increase the production capacity and the heat economy of spray drying apparatuses and processes of the above defined type and to facilitate operation thereof.

Further objects and advantages will appear form the below description.

Summary of the Invention.

It has turned out that said objects may be achieved by conducting the recycling of the fine particles to the spray drying chamber in a special way as explained below.

Thus the invention deals with a process for producing

an agglomerated powder by spray drying a liquid in a drying chamber of which the lower part is formed by a conical downward tapering section, including the steps of atomizing said liquid in the upper part of the drying chamber into at least one downward first stream of drying gas to produce particles, withdrawing a stream of spent drying gas from at least one-location in the upper part of the drying chamber together with entrained fine powder particles thereby creating a drying gas flow having an outward and upward turning portion in the conical chamber section, collecting said fine powder particles from the thus withdrawn stream of spent drying gas, and recycling them to the drying chamber, and recovering agglomerated powder product of low dust content from the bottom of the chamber.

According to the invention the improvement comprising recycling of said fine particles to the drying chamber by pneumatic injection thereof from a location in the lower part of the drying chamber and in one or more directions forming an angle of 0-90° to the upward center axis of the chamber, to utilize said outward and upward turning portion of the drying gas flow to introduce the fine particles evenly in a horizontal, annular zone near the wall of the conical section of the chamber.

By performing the recycling of the fine particles as an upward axial and/or slanting outward injection in the lower conical section of the drying chamber, preferably in the lower half of said section, it is ensured that an even and substantial concentration of fines will be present in the chamber at the location where such an even and substantial fines concentration is most advantageous to obtain an efficient agglomeration and an improved drying, permitting better heat economy since a reduction of drying air temperature and a higher relative humidity can be tolerated without operational problems caused by depositing of sticky moist powder on the chamber walls. The efficient agglomeration is reflected in the formation of strong agglomerates and a very low proportion of dust in the final product.

The above beneficial effect of recycling fine particles by injecting them as defined above may be explained by computer simulation using the software "Fluent", obtainable from Fluent Inc., Hannover, New Hampshire, US. By said computer simulating technique it is possible to establish that a maximum concentration of moist but not wet particles having a stickiness suitable for catching fines to form agglomerates of desired strength, exists in the chamber in an annular zone adjacent to the wall of the conical section.

By recycling said fines in a predominantly upward direction from a site above the center of the fluidized layer the fines meet the above-mentioned first stream of drying gas at a location where it is loosing its downward velocity and is diverted outward against the conical chamber wall, as explained in more details below.

By means of this diverted flow of drying gas possibly admixed with gas from an integrated fluidized layer, if present, the fines are carried exactly to the zone near the upper part of the conical chamber wall portion where the concentration of moist particles is high and consequently the chances for agglomerate-forming collision is good.

If, alternatively, the injection of fine particles is made at larger angles to the upward center axis, which means in more horizontal directions, the fine particles are blown more directly to the zone where their effect on the drying and agglomeration is most beneficial.

Said zone near the upper part of the conical chamber wall is the area in the chamber where the risk for formation of sticky deposits on the chamber wall is most pronounced, due to the high particle concentration in said zone. Therefore, it is particularly advantageous that the fines are carried to said zone and distributed evenly therein, since the presence of fine dry particles has a protecting effect against adhering chamber wall deposits.

In comparison with prior art systems in which fine particles are recycled to the upper part of the drying

chamber, the present process further has the advantage of avoiding heat damage of the fine particles in the hot zone of the drying chamber.

The present process has been developed mainly in connection with the use of drying apparatuses having an integrated fluidized layer and consequently a preferred embodiment is one, in which a layer of particles is kept fluidized at the bottom of the drying chamber by introduction of a second stream of drying gas through a perforated supporting plate, in which process a pneumatic injection of the fine particles is made from a position between the upper surface of the fluidized layer and halfway up to the top of the chamber.

The atomizing of the liquid to be spray dried is preferably performed by using at least one downward directed nozzle or a rotary atomizer. In the embodiments, where a fluidized layer is maintained in the bottom of the drying chamber most experience exists with nozzle atomization, which is therefore preferred in said embodiments.

In a preferred embodiment the pneumatic injection of the fine particles is accomplished through a vertical pipe debouching in the lower half of the frusto-conical section of the drying chamber.

The upward stream of fine particles then meets the central downward stream of drying gas at a location where it is loosing its downward velocity and is diverted outward against the conical chamber wall to obtain optimal conditions for agglomeration and to protect the chamber walls from contact with moist particles which might cause deposits.

Thereby improved product quality, production capacity and heat economy are obtained as explained in connection with the below descriptions of the embodiments depicted in on the drawing.

Whether the drying chamber is provided with an integral fluidized layer or not, it is often advantageous

to recover the agglomerated powder from the bottom of the drying chamber at a moisture content higher than the one desired for the final product and to subject the thus recovered moist powder to a supplementary drying in a fluidized or moving bed outside the drying chamber. Such a drying may be combined with a cooling process and with dust removal by using a drying or cooling air with a velocity such that the fine particles are blown off from the layer of agglomerated particles.

The agglomerated product recovered from the drying chamber may also be subjected to treatment in a gravitational countercurrent classifier to reduce the content of dustforming fine particles therein.

The fine particles separated from the product fraction either in an extraneous fluidized bed or in a gravitational classifier may be recycled to the drying chamber together with the fine particles collected from the stream of drying gas withdrawn at the top of the drying chamber or alternatively they may, to reduce the amount of fine particles to be recycled to the drying chamber, be added to the feed liquid before atomization thereof.

The fact that recycling of the fine particles by the process according to the present invention counteracts formation of harmful deposits on the chamber wall, enables operation of the drying chamber at a higher relative humidity than would have been possible with conventional recycling systems.

Since operation at higher relative humidity enables energy savings a preferred embodiment of the process is characterized in, that the amount, temperature and concentration of the liquid which is atomized as well as the amount and temperature of drying gas are adjusted to obtained a relative humidity of the stream of spent drying gas withdrawn from the chamber substantially higher than the maximum relative humidity allowable if fine particles were recycled using the conventional procedures therefore.

As mentioned above, the preferred means for

reintroducing the fine particles in the drying chamber is an upward directed pipe debouching under the location where the downward stream of drying gas is loosing its downward velocity. A convenient mode for establishing where this happens is by means of computer simulation.

Alternatively, the introduction of the particles to be recycled can take place by means which direct the fine particles more directly towards the chamber walls, which means may be stationary or mobile, for instance rotatable utilizing the energy of the pressurized gas serving as transportation gas for the fine particles to rotate a nozzle-like member.

The invention further comprises a spray drying apparatus suitable for producing an agglomerated powder by the process according to the invention, said apparatus having a drying chamber, the lower part of which is formed by a conical downward tapering section, means for atomizing a liquid into an atomizing zone in the upper part of the chamber, drying gas distributing means for directing at least one first stream of drying gas downward around the atomizing means, means for withdrawing an agglomerated powder from the bottom of the chamber, outlet means in the top of the chamber for withdrawing a stream of spent drying gas and entrained fine particles, and means for collecting said fine particles and reintroduction thereof into the drying chamber, characterized in that said means for reintroducing said fine particles into the chamber comprises means for pneumatic injection of the fine particles in the lower part of the drying chamber and in one or more directions forming an angle of 0-90°C to the upward center axis of the chamber to introduce said fine particles evenly in a horizontal annular zone near the wall of the conical section of the chamber by utilizing an outward and upward drying gas flow existing in the lower part of the drying chamber during the operation of the apparatus.

A preferred embodiment of said apparatus comprises means for maintaining a fluidized particle layer at the

bottom of the chamber including a perforated plate for supporting said layer and means for introducing a second stream of drying gas below said perforated plate and means for recycling fine particles debouching above the level of the surface of the fluidized layer during operation but at smaller distance to said level than to the top of the chamber.

The process and the apparatus according to the invention may be utilized for producing a large variety of agglomerated powders including technical products, such as dyestuffs and products of the food industry, such as soup powders, milk products, etc.

Brief Description of the Drawing.

The invention is further explained below with reference to the drawing in which

Fig. 1 very schematically depicts an embodiment of a plant suitable for performing the invention, said embodiment comprising an integrated fluidized particle layer at the bottom of the spray drying chamber, and

Fig. 2 depicts an embodiment similar to the one shown in Fig. 1 but having a different system for aftertreatment of the produced agglomerates and utilization of the fine particles separated therefrom.

Description of Preferred Embodiments.

In Fig. 1 of the drawing a spray drying chamber 1 is shown having an upper cylindrical section 2 and an underlaying section 3 of frusto-conical shape.

At the top of the chamber an atomizer 4, in the depicted embodiment a nozzle, is arranged for atomizing a liquid feed supplied through conduit 5. In the ceiling the chamber also has a gas distributor 6 receiving hot drying gas through conduit 7.

From the gas distributor 6 a first stream of drying gas, typically drying air, is directed downwards around the atomizer 4, and the droplets ejected therefrom are by said

first stream of drying gas carried downwards centrally in the chamber as shown on the drawing, and at the same time an evaporation takes place from the droplets which are thereby converted into moist solid particles.

At the bottom portion of the drying chamber a perforated supporting plate 8, is arranged, below which a secondary stream of drying gas is introduced through conduit 9. Above said plate 8 a fluidized layer 10 is maintained consisting of particles formed in the upper part of the chamber by partial drying of the atomized droplets.

The secondary stream of drying gas introduced through 9 passes the perforated plate 8 and the fluidized layer 10, from where it leaves to the drying chamber entraining the fine, non-agglomerated particles from said fluidized layer.

A stream of gas comprising the gas introduced through 7 and 9 as well as vapours formed by the drying, and auxiliary gas are together with a substantial amount of entrained fine particles withdrawn from the ceiling of the chamber through ducts 11 and conducted to a cyclone 12. From said cyclone the gas is conducted with a reduced particle content through a baghouse filter 13 for collecting nearly all the remaining particles in the gas stream.

The particles recovered in the cyclone 12 and in the baghouse filter 13 are, according to the invention, pneumatically recycled to the drying chamber 1 through a pipe 14 which debouches above a fluidized layer at a central site in the frusto-conical section 3 of the drying chamber, preferably in the lower half part of said section.

From the fluidized layer 10 a product is continuously withdrawn to an external after-drying unit 15, preferably a vibrated fluidized bed apparatus, wherein a further drying and cooling are performed. The depicted embodiment receives drying gas in a first section through conduit 16 and cooling gas through conduit 17.

The spent drying and cooling gas which leaves the unit 15 contains a minor amount of entrained fine dustforming particles and are therefore let to the cyclone as

shown.

Alternatively, the fine particles entrained by the gas leaving the unit 15 may be recovered from said gas by a separate cyclone, filter or wet scrubber and used for preparing the liquid to be introduced through conduit 5. This alternative arrangement is not shown on Fig. 1.

The final product consisting essentially of relatively large, strong agglomerates having the desired particle size and which has only a very small content of dustforming particles is recovered from unit 15 through conduit 18.

As schematically indicated on the drawing, the downward flow of the first stream of drying gas in the chamber 1 is diverted towards the chamber walls at a certain level of the frusto-conical section 3 of the chamber. This is partly a result of the influence of the upward flow (not shown on the drawing) of the second stream of drying gas passing through the fluidized layer but this characteristic flow pattern also exists in spray drying chambers operating without secondary drying gas being introduced in the bottom, as long as the introduction and withdrawal of the primary drying gas are as specified above.

The fine particles recycled to the chamber via the pipe 14 meets the first stream of drying gas with entrained moist particles at the place where said first stream diverts or turns direction towards the conical chamber walls. By this diverted or deflected gas stream the fine particles are carried to an annular zone very near the conical walls and, dependent on the general shape of the chamber in the vicinity of the level where the upper part of the conical wall meets the cylindrical wall. On the drawing said zone is indicated by arrows marked A.

In contrast to what has hitherto been assumed, the zone A is the place where the concentration of particles having a uniform moisture content and a suitable stickiness for forming agglomerates with the fine particles, is higher than in most other parts of the drying chamber above the

fluidized layer.

A substantial part of the moist powder produced by the drying of the atomized droplets and entrained with the stream of drying gas collects on the conical chamber walls in admixture with the recycled fine particles. Due to the features characteristic for the invention these particles are carried just to the zone where said moist powder collects, and the presence of these relatively dry fine particles makes it possible for said powder to collect in a quite moist state without adhering to the chamber walls.

The thus formed mixture of relatively dry recycled fine particles and moist particles resulting from only partially dried atomized droplets slides down into the fluidized bed wherein it is further dried, and solid agglomerates of particles having fixed positions in relation to each other are formed.

For several reasons, including heat economical considerations well known to the skilled person, it is desired in drying processes of the present type to perform as large a portion of the drying as possible in the fluidized bed layer.

The present process enables fulfilment of this desire to a higher extent than do comparable prior art processes.

As an alternative to the embodiment shown in Fig. 1 having a fluidized layer at the bottom of the drying chamber, the apparatus may operate without such a fluidized layer and in this case the product is recovered from the lowest part of the conical section which is typically provided with a rotary lock valve. In this embodiment which is not shown on the drawing the pipe for recycling the fine particles may pass through the conical wall of the drying chamber and bend upwards to deliver the fine particles as specified in the above description of the present invention.

On the drawing Fig. 2 depicts an alternative version of the process in which the agglomerates recovered from the fluidized layer 10 pass through a horizontal countercurrent

classifier 19. Through the passage the agglomerate product is cooled and substantially freed from dustforming fine particles and is recovered through 20, whereas the fine particles entrained by the cooling gas is conducted to a cyclone 21 from where the fine particles are withdrawn through conduit 22 and let to a (not shown) plant for manufacturing the feed liquid to be introduced to the atomizer through conduit 5. Alternatively the fine particles withdrawn through 22 or a part thereof may be recycled to the chamber 1 together with the fine particles recovered in 12 and 13.

From the explanation presented with reference to Fig. 1 above it will be understood that introduction of the fine particles as specified involves considerable advantages over prior art processes where recycling is made either to the upper part of the drying chamber near the atomizer or in the bottom of the chamber into the fluidized bed or tangentially. Said advantages will be further substantiated in the Examples below.

The invention will be further explained with reference to the following example.

EXAMPLE

A series of tests was conducted in a plant essentially corresponding to the one depicted in Fig. 1.

The spray drying chamber had a diameter of 2.0 meter, a cylindrical hight of 2.3 meter and a cone angle of 40°.

Besides the arrangement for reintroduction of the fine particles according to the present invention as shown in Fig. 1, the spray drying chamber was equipped with means for injecting the fine particles near the atomizer nozzle 4 or tangentially to the upper part of the conical chamber walls as conventional.

Further the chamber was equipped with pneumatic hammers to counteract depositing of moist powder on the chamber walls.

The product from the integrated fluidized layer was

passed through two 0.3 m^2 vibrated fluid beds acting as coolers before bagging off.

In all tests the feed to be spray dried was an aqueous solution of maltodextrine of 38 percent by weight dry solids prepared by dissolving maltodextrine in demineralized water and keeping the solution overnight without stirring for release of air bubbles.

A total of 10 tests were made. Tests 1-5 were made with recycling of the fine particles to the nozzle or to the cone walls and thus represent the conventional prior art technique.

Tests 6-10 were run according to the present invention and the fine particles were injected pneumatically upward from a pipe debouching 2 m above plate (tests 6 and 7) or 0.75 m above plate (tests 8-10).

The most important of the operational parameters and characteristics of the product obtained appear from the following table:

Test No.	Locations for fines injection	Feed rate kg/h	Primary drying air		Drying air to integrated fluidized layer		Mixed spent drying air		Product from integrated fluidized layer		
			rate kg/h	Temp. °C	kg/h	Temp. °C	Temp. °C	Rel.hum. %	moisture %	D[v,0.5]µm	Span
1	nozzle	95	1440	227	578	80	93	8.6	-		
2	cone walls	95	1424	198	578	81	80	14.1	2.54	152	1.11
3	nozzle	97	1440	198	578	81	77	15.8	3.37	170	1.51
4	cone walls	97	1440	200	578	80	79	14.8	3.04	178	5.39
5	nozzle (modified) 1)	98	1440	199	589	81	81	13.4	4.53	180	3.71
6	2 m above plate	98	1450	201	585	77	81	13.3	2.85	151	1.14
7	2 m above plate	99	1450	182	484	76	70	21.4	5	157	1.10
8	0.75 m above plate	101	1460	179	481	77	69	23.5	-	-	-
9	0.75 m above plate	98	1450	170	479	76	64	27.8	6.33	173	1.08
10	0.75 m above plate	98	1453	159	483	77	62	30.3	7.82	186	1.07

1) via a cyclone around the nozzle

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To supplement the information deducible from the table, the following remarks should be made to the tests:

Test 1. The product comprised a fraction of very large agglomerates which were over-wetted.

Test 2. Very small loose deposits in the cone tip of the chamber. Not critical but the plant was on the limit for steady state running.

Test 3. As in test 1 agglomerates which had been over-wetted or were still to wet were present, deposits as in test 2.

Test 4. Deposits as in test 2.

Test 5. In this test where the fines were recycled via a cyclone around the nozzle over-wetted and wet agglomerates as well as deposits were found as in test 2.

Tests 6-10. In these tests, which represent the process according to the invention, the recycling is performed through a 50 mm vertical pipe located as specified in the table.

While maintaining the feed rate between 98 and 101 kg/h it was found possible to reduce the inlet temperature to 159°C and the outlet temperature to 62°C, as it appears from the table, at steady state conditions and without critical deposits. At the same time the relative humidity of the mixed spent drying air was increased to 30.3%. There were no over-wetted or wet agglomerates in the product.

The fact that the process can be operated with such a high relative humidity in the mixed drying air leaving the drying chamber reflects the efficiency of the process and the improved heat economy obtainable therewith.

The D[v,0.5]µm values of the table show that the particle size of the product agglomerates is in the desired range, and the Span values show that the agglomerate size distribution is excellent for the product of the tests 6-10.

PATENT CLAIMS

1. A process for producing an agglomerated powder by spray drying a liquid in a drying chamber of which the lower part is formed by a conical downward tapering section, including the steps of atomizing said liquid in the upper part of the chamber into at least one downward first stream of drying gas to produce particles, withdrawing a stream of spent drying gas from at least one non-central location in the upper part of the drying chamber together with entrained fine powder particles, thereby creating a drying gas flow having an outward and upward turning portion in the conical chamber section, collecting said fine powder particles from the thus withdrawn stream of spent drying gas, and recycling them to the drying chamber, and recovering an agglomerated powder product from the bottom of the chamber, c h a r a c t e r i z e d in that the recycling of said fine particles to the drying chamber is performed by pneumatic injection thereof from a location in the lower part of the drying chamber and in one or more directions forming an angle of 0-90° to the upward center axis of the chamber, to utilize said outward and upward turning portion of the drying gas flow to introduce the fine particles evenly in a horizontal, annular zone near the wall of the conical section of the chamber.

2. The process of claim 1 in which a layer of particles is kept fluidized at the bottom of the drying chamber by introduction of a second stream of drying gas through a perforated supporting plate, c h a r a c t e r i z e d in that the pneumatic injection of the fine particles is made from a position between the upper surface of the fluidized layer and halfway up to the top of the chamber.

3. The process of claim 1 or 2, wherein the atomizing of the liquid is performed by using at least one downward directed nozzle or a rotary atomizer.

4. The process of claim 1, 2 or 3, wherein the pneu-

matic injection of the fine particles is accomplished through a vertical pipe debouching in the lower half of the conical section of the drying chamber.

5. The process of any of the preceding claims, wherein the agglomerated powder recovered from the bottom of the drying chamber is subjected to a drying and/or cooling in a fluidized or moving bed.

6. The process of any of claims 1-4, wherein the agglomerated powder recovered from the drying chamber is subjected to a treatment in a gravitational countercurrent classifier to reduce the content of dustforming fine particles therein.

7. The process of any of the preceding claims, wherein the amount, temperature and concentration of said liquid atomized as well as the amount and temperature of drying gas are adjusted to obtain a relative humidity of the stream of spent drying gas withdrawn from the chamber substantially higher than the maximum relative humidity allowable if fine particles were recycled using the conventional procedures therefor.

8. The process of any of the preceding claims, wherein the place for introduction of recycled fine particles into the drying chamber is below the level where the central part of the downward first stream of drying gas has substantially lost its downward velocity and is turning outward.

9. The process of claim 8, wherein said level where the central part of the downward first stream of drying gas has substantially lost its downward velocity is estimated by using computer simulation.

10. A spray drying apparatus having a drying chamber (1), the lower part of which is formed by a conical downward tapering section (3), means (4) for atomizing a liquid into an atomizing zone in the upper part of the chamber, drying gas distributing means (6) for directing at least one first stream of drying gas downward around the

atomizing means, means for withdrawing an agglomerated powder from the bottom of the chamber, outlet means (11) in the top of the chamber for withdrawing a stream of spent drying gas and entrained fine particles, and means for collecting said fine particles (12,13) and reintroduction thereof into the drying chamber, c h a r a c t e r i z e d in that said means for reintroducing said fine particles into the chamber comprises means (14) for pneumatic injection of the fine particles in the lower part of the drying chamber and in one or more directions forming an angle of 0-90°C to the upward center axis of the chamber (1) to introduce said fine particles evenly in a horizontal annular zone (A) near the wall of the conical section (3) of the chamber by utilizing an outward and upward drying gas flow existing in the lower part of the drying chamber during the operation of the apparatus.

11. An apparatus according to claim 10 comprising means for maintaining a fluidized particle layer (10) at the bottom of the chamber (1) including a perforated plate (8) for supporting said layer and means (9) for introducing a second stream of drying gas below said perforated plate, and means for recycling said fine particles debouching above the level of the surface of the fluidized layer during operation but at smaller distance to said level than to the top of the chamber.

12. An apparatus according to claim 10 or 11, wherein said means for recycling the fine particles to the drying chamber comprises a central upward directed pipe debouching in the lower half of the conical section of the chamber.

13. An apparatus according to claim 10-12, wherein the means for atomizing the liquid is selected between a two-fluid nozzle, a pressurized nozzle and a rotary atomizer.

14. An apparatus according to any of claims 10-13 having a vertical gravitational classifier which is connected to said means for withdrawing powder from the

bottom of the spray drying chamber, the upper end of said classifier being connected to a particle separator (21) for recovering fine particles, and the bottom portion of said classifier having an outlet for product agglomerate particles and an inlet for classifying gas.

15. An apparatus according to claim 14, wherein the particle separator is connected to means for conducting the particles recovered therein to the feed liquid to be atomized and/or to the chamber (1) together with the fine particles recovered in the collecting means (12,13).

FIG. 1

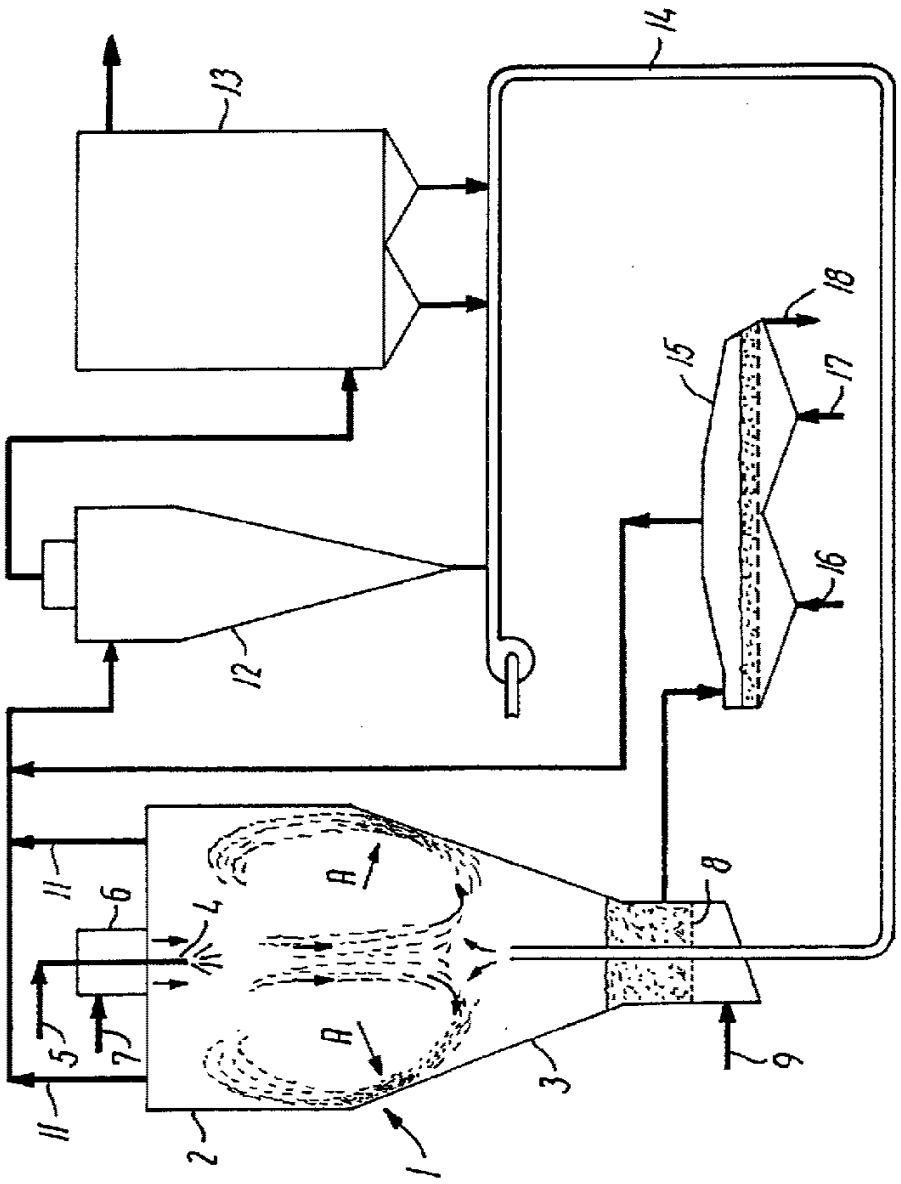
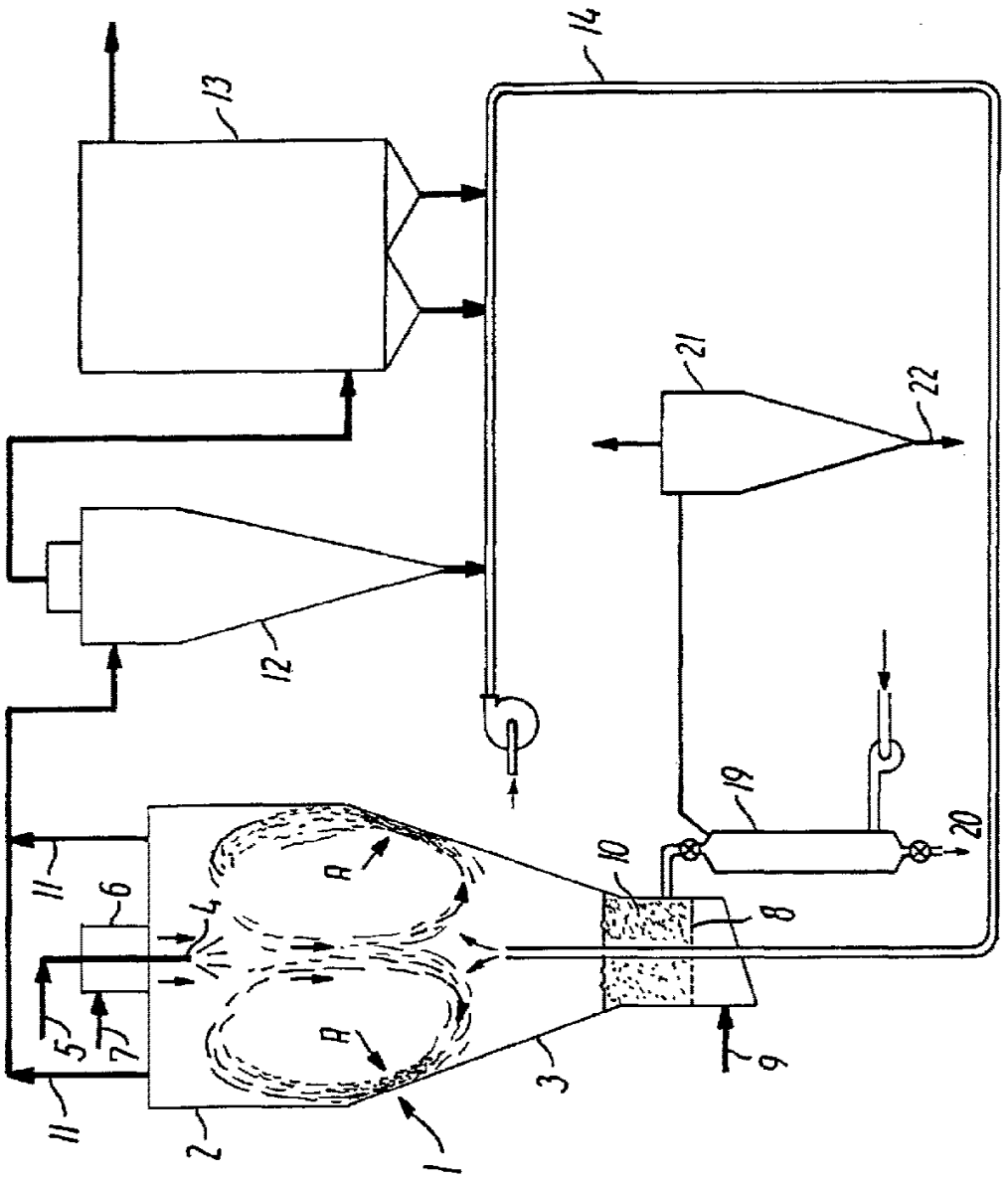


FIG.2



INTERNATIONAL SEARCH REPORT

Inter. .onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J2/04 B01J2/16 B01D1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 378 498 (A/S NIRO ATOMIZER) 18 July 1990 cited in the application see page 4, line 51 - page 5, line 17; figure 2 ---	1-3,5,6, 10,11, 13-15
Y	EP,A,0 097 484 (A/S NIRO ATOMIZER) 4 January 1984 see page 15 - page 17; figure ---	1,3,5,6, 10,13-15
Y	FR,A,2 143 306 (ALLIED CHEMICAL CORPORATION) 2 February 1973 see page 7, line 16 - page 8, line 27; figure ---	2,11
A	GB,A,1 026 329 (DOW CHEMICAL COMPANY) 13 August 1964 see the whole document --- -/--	1,2,6,7, 10

[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 May 1994	30. 05. 94

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 338 470 (SOCIETE LAB) 12 August 1977 see page 3 - page 7; figure 1	1,4,8,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No
PCT/DK 93/00376

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EP-A-0378498	18-07-90	AU-B-	623967	28-05-92
		AU-A-	4776390	12-07-90
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		DE-A-	2230158	28-12-72
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(54) Title: PROCESS FOR MAKING LAXATIVES CONTAINING DIOCTYL SULFOSUCCINATE

(57) Abstract

A process is described for making an ingestible, neutral tasting laxative composition by coating dioctyl sulfosuccinate with a material selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, sucrose polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, and combinations thereof. Preferably, two successive, different coatings are applied to the dioctyl sulfosuccinate by steps including either fluid bed coating, spray congealing, spray quenching, or spray drying.

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PROCESS FOR MAKING LAXATIVES CONTAINING DIOCTYL SULFOSUCCINATE

BACKGROUND OF THE INVENTION

Bulk fibers such as psyllium and methylcellulose are known effective laxatives. Bulk fiber laxatives are often powders which are mixed in water and consumed. Another type of laxative is a stimulant laxative, which is typically available in tablet or capsule form. These include senna, phenolphthalein, casanthranol, and bisacodyl.

Benefits of bulk laxatives relative to stimulant laxatives include: mildness, naturalness, minimal to no diarrhea, and/or a more normal, bulked bowel movement. However, bulk laxatives traditionally work slower than stimulant laxatives. Although stimulant laxatives can be harsh and are sometimes associated with cramping, the constipated person is often quite uncomfortable and does not want to wait the several days it may take for a bulk fiber to provide relief. Stimulant laxatives ordinarily provide overnight relief from constipation. An ideal laxative would be one which provides the benefits of bulk fiber, yet also provides speed to relief.

The active ingredient in some commercially available stool softeners is dioctyl sulfosuccinate, which is an anionic medicinal surfactant. Dioctyl sulfosuccinates combined with stimulant laxatives such as phenolphthalein, casanthranol, and senna are permitted active ingredients, according to the Federal Register, vol. 40, No. 56, Part II Over-the-Counter-Drugs, "Proposed Establishment of Monographs for OTC Laxative, Antidiarrheal, Emetic and Antiemetic Products", p.12941. Also included therein is dioctyl sulfosuccinate (docusate sodium) in combination with sodium carboxymethylcellulose. It is believed that there is no commercially available laxative composition with both dioctyl sulfosuccinate and the bulk fibers herein as the active ingredients.

It has been found by the present invention that bulk fibers, particularly psyllium, methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, and mixtures thereof, can be combined with dioctyl sulfosuccinate to provide a laxative with surprisingly increased speed to relief. Benefits of this combination can include gentle relief, making bowel movements easier to pass, relief of constipation, causing predictable results, good signal to go, complete relief and/or a normal, bulked bowel movement.

A problem, though, with including dioctyl sulfosuccinate in ingestible laxative compositions, particularly those which are to be masticated, is the bad taste of this anionic surfactant. This bitter taste is a particular problem in laxative drink mixes, chewable tablets and food forms containing dioctyl sulfosuccinate. A process has therefore now been invented by which can been invented by which an ingestible, neutral tasting laxative composition containing dioctyl sulfosuccinate can be made.

This process has the advantage of making a composition which is effective for treating constipation, and which, even though it contains dioctyl sulfosuccinate, is not bad tasting. By this process, the encapsulated dioctyl sulfosuccinate is not tasted in the mouth, yet it is available in the gastrointestinal tract to aid in the relief of constipation.

A further advantage of this process is its use in making a dioctyl sulfosuccinate-containing composition for use as a medicinal drug which minimizes or eliminates the stomach disturbances, such as nausea, which can be side effects of taking dioctyl sulfosuccinate.

SUMMARY OF THE INVENTION

This invention relates to a process for making an ingestible, neutral tasting laxative composition by coating dioctyl sulfosuccinate with a material selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, sucrose polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, and combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

I. Composition of the Present Invention

Compositions according to the present invention include certain bulk fibers and dioctyl sulfosuccinate. Bulk forming laxatives work by increasing the water content and bulk volume of the stool, thereby promoting a bowel movement. The bulk fiber is generally not absorbed by the gastrointestinal tract. Dioctyl sulfosuccinate assists in relieving constipation. The combination is believed to work more quickly to relieve constipation than bulk fiber alone. The bulk fiber ingredient of the present compositions ordinarily is a powder which comprises the physical majority of the composition. The dioctyl sulfosuccinate is ordinarily a soft, waxy material which is present in the composition in much smaller amounts than the bulk fiber.

A. Bulk Fiber

The ingestible compositions herein comprise from about 1% to about 99.99%, preferably from about 5% to about 99%, more preferably from about 10%

to about 98%, most preferably from about 15% to about 95%, by weight of the composition, of bulk fiber. For the preferred drink mix form, from about 50% to about 70%, by weight of the composition, of bulk fiber, preferably psyllium, is preferred.

Preferred bulk fibers herein are selected from the group consisting of psyllium, methylcellulose, calcium polycarbophil, polycarbophil, bran, malt soup extract, karaya, guar gum, and mixtures thereof. More preferred bulk fibers are selected from the group consisting of psyllium, sodium methylcellulose, calcium polycarbophil, polycarbophil, and mixtures thereof. Most preferred is psyllium husk. The bulk fiber herein is preferably not carboxymethylcellulose. Carboxymethylcellulose has a tendency to make smeary stools, which are difficult to wipe clean after a bowel movement.

Preferred psyllium husk for use herein comprises particle sizes distributed such that: less than about 15% is greater than about 80 mesh, at least about 45% is within the range of from about 80 mesh to about 200 mesh, and less than about 40% is smaller than about 200 mesh. This is according to U. S. Patent 5,149,541, Leis, Jr. et al, issued September 22, 1992, incorporated herein by reference. Most preferably, the psyllium husk is milled to a particle size no greater than 4% on 100 mesh and betwen 25% and 50% through 200 mesh.

Preferred psyllium husk for use herein is sanitized according to U. S. Patents 4,911,889 and/or 5,229,117, Leland et al, issued March 27, 1990 and July 20, 1993, both incorporated herein by reference. Psyllium husk for use herein is preferably in a composition comprising hydrolyzed starch oligosaccharide, preferably maltodextrin, and is preferably sweetened with cyclamate, aspartame, saccharin or a combination thereof, according to U. S. Patent 4,459,280, Colliopoulos, issued June 10, 1984, incorporated herein by reference. Psyllium husk for use herein preferably comprises edible acid and is agglomerated according to U. S. Patent 5,219,570, Barbera, issued June 15, 1993, incorporated herein by reference. The psyllium husk preferably comprises citric acid which is uniformly dispersed throughout a maltodextrin coating, further according to Barbera. Preferably, then, the psyllium husk is agglomerated with maltodextrin and further comprises citric acid which is uniformly dispersed throughout the maltodextrin.

Preferably, psyllium husk-containing drink mixes herein comprise the divalent cation salt of strong inorganic acids selected from the group consisting of magnesium sulfate, calcium sulfate, calcium chloride, zinc sulfate, zinc chloride, and mixtures thereof, preferably magnesium sulfate. This is according to U. S. Patents 5,232,698

and/or 5,234,916, Hord, issued August 3 and 10, 1993, both incorporated herein by reference.

B. Dioctyl Sulfosuccinate

The ingestible compositions herein also comprise from about 0.0005% to about 25%, preferably from about 0.005% to about 15%, more preferably form about 0.1% to about 10%, most preferably from about 0.5% to about 5%, by weight of the composition, of dioctyl sulfosuccinate.

Preferably, the dioctyl sulfosuccinate is selected from the group consisting of dioctyl sodium sulfosuccinate, dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, and mixtures thereof. Most preferred is dioctyl sodium sulfosuccinate or dioctyl calcium sulfosuccinate. This composition is preferably a single dose composition for relieving constipation.

Dioctyl sulfosuccinate is sulfosuccinic acid bis[2-ethylhexyl]ester. Sodium dioctyl sulfosuccinate is a white waxy solid producing a clear, colorless solution in alcohol.. The chemical formula for sodium dioctyl sulfosuccinate is $C_{20}H_{37}O_7SNa$.

The mechanism of action of dioctyl sodium sulfosuccinate has not been proven. Without meaning to be bound by theory, it is believed that dioctyl sodium sulfosuccinate at millimolar concentrations provides laxation by acting as an intestinal secretagogue. It is further believed that the ability of dioctyl sodium sulfosuccinate to enhance retention of luminal fluid and therefore fecal hydration may be the reason that it enhances laxation when combined with bulk fiber, particularly psyllium husk. Dioctyl sodium sulfosuccinate is not appreciably absorbed from the gastrointestinal tract.

Interestingly, dioctyl sodium sulfosuccinate is a medicinal drug which has been found to be commonly associated with gastrointestinal disturbances such as diarrhea in both hospitalized and nonhospitalized patients, according to R. Stewart and L. Cluff, "Gastrointestinal Manifestations of Adverse Drug Reactions", The American Journal of Digestive Diseases, Vol. 19, No. 1, pp. 1-7 (January 1974). The bulk fibers herein may reduce these gastrointestinal disturbances.

The combination of a natural stimulant laxative, casanthranol, and dioctyl sodium sulfosuccinate has been found to be significantly superior to a preparation containing another natural stimulant laxative, senna, in producing earlier stools with less straining. M. J. Adels, "Relative Efficacy of Three Laxatives in Post-Partum Hospital Use", Delaware Medical Journal, July, 1974.

C. Forms

The laxative composition herein is preferably selected from the group consisting of a drink mix, solid dose form, gel capsule form, and a food form. It is

most preferably in the form of a drink mix. Food forms include wafers, bars, cookies, cereals, muffins, beverages and baked goods where moisture contents are kept at very low levels. For baked goods, it is preferred to keep the water activity (a_w) less than 0.5. Preferred food forms herein are wafers or bars.

Solid dose forms include tablets, liquid containing capsules, and hard or soft shelled capsules. Gel capsule forms can include hard or soft gelatins, which can be filled with dry or liquid materials.

The laxative compositions herein are preferably selected from the group consisting of drink mixes, tablets, capsules, liquicaps, wafers, and bars. They are most preferably powdered drink mixes. The most preferred drink mixes herein consist essentially of from about 4 grams to about 10 grams, most preferably from about 4.5 grams to about 6 grams, of bulk fiber, preferably psyllium husk, and from about 100 milligrams to about 500 milligrams, most preferably from about 200 milligrams to about 300 milligrams, of dioctyl sulfosuccinate, preferably calcium or sodium.

Alternatively, the compositions herein can be in two or more parts or phases, as where dioctyl sulfosuccinate is in microcapsules within or combined with the bulk fiber.

Compositions herein can be used for treatment of occasional constipation, eg. a single dose, or for daily fiber therapy, eg. a drink mix which is mixed with at least eight ounces of liquid and ingested one time per day each morning for no more than seven days. Single doses are preferred.

A single dose of a composition herein preferably contains from about 0.5 gram to about 100 grams, preferably from about 1 to about 10 grams, of bulk fiber, preferably psyllium husk. A single dose of a composition herein also preferably contains from about 5 milligrams to about 1000 milligrams, preferably from about 100 milligrams to about 500 milligrams, of dioctyl sulfosuccinate, preferably calcium or sodium.

D. Optional Ingredients

Compositions of the present invention optionally contain additional ingredients, depending upon the form of the composition and the desired effect and aesthetics. Some compositions, such as solid dose forms, gel capsule forms and food forms, preferably comprise, in addition to the bulk fiber and dioctyl sulfosuccinate, from about 0.1% to about 85%, more preferably from about 30% to about 80%, most preferably from about 50% to about 70%, by weight of the composition, of carrier material. Such carrier material can include flow agents, like fumed silicon dioxide, starches, dextrin, maltodextrins, sweeteners, dispersants, emulsifiers,

flavoring, coloring, and contain other fibers, such as oat bran, wheat bran, or rice bran, to add body and flavor.

Psyllium-containing product forms, methods for making, and useful carrier materials are described in, for example, U. S. Patent 4,459,280, Colliopoulos, issued July 10, 1984, U. S. Patent 4,548,806, Colliopoulos, issued October 22, 1985, and U. S. Patent 4,321,263, Powell et al, issued March 23, 1982, all incorporated herein by reference.

Useful excipients which can be included in pharmaceutical forms herein are described in the American Pharmaceutical Association's Handbook of Pharmaceutical Excipients, incorporated herein by reference.

E. Methods for Treating Constipation

The present invention also relates to methods for treating constipation in humans or lower animals. These methods comprise orally administering a safe and effective amount of any of the laxative composition described herein.

By "safe and effective amount" is meant an amount of this laxative composition which is high enough to positively modify the condition being treated, but low enough to avoid serious side effects at a reasonable benefit/risk ratio within the scope of sound medical judgement. The safe and effective amount may vary with the age and physical condition of the person being treated, the severity of the condition, the specific ingredients employed, and like factors.

II. Process of the Present Invention

The present invention is a process for making an ingestible, neutral tasting laxative composition by coating dioctyl sulfosuccinate with a material selected from the group consisting of C14-18 fats, C16-20 fatty acids, polyol polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, and combinations thereof. Derivatives of these materials are also included, though not preferred.

By "neutral tasting" is meant that, when ingested, the bitterness of the dioctyl sulfosuccinate is not detected by the person (or lower animal) who is ingesting it (ie. the taste is not bad). A sugar or other flavor could also be added to the composition to enhance its taste. These compositions are preferably chewable tablets, drink mixes, and food forms.

A. Benefits of Coating

The coating of the present process is advantageous in that the dioctyl sulfosuccinate is prevented from effecting a bad taste in the mouth. The coating can also be chosen so that it remains largely intact through the stomach, thereby avoiding the gastric disturbances which are commonly associated with the use of dioctyl sulfosuccinate as a medicinal drug. The protective coating is chosen so that it is

dissolved/melted/digested before reaching the large intestine so that dioctyl sulfosuccinate is available for stool softening action.

For example, a C_{14-18} fat coating on the dioctyl sulfosuccinate is believed to melt in the gastrointestinal tract, releasing the dioctyl sulfosuccinate to soften the stool. Fat micelles are then believed to be digested by pancreatic lipase in the small intestine, and the free fatty acids and monoglycerides thus released are then almost totally absorbed through the wall of the small intestine. In the case of the fat/wax coating, it is believed that when the fat is melted, the wax, which is bound by the fat, is also released. It is likely that the wax is passed through with the stool. In the case of a fatty acid coating, the fatty acids melt in the gastrointestinal tract and the dioctyl sulfosuccinate is then released to act in the intestine. The fatty acids are easily absorbed by the small intestine.

The pH sensitive polymer and gum coatings herein have the advantages of the fat/fatty acid coating. It is believed that the pH sensitive polymer coating does not dissolve until it is in a specific pH environment, preferably the basic environment of the small intestine. It is likely that the pH sensitive polymer is passed through with the stool. The food gums also "melt away" in the gastrointestinal tract, releasing the dioctyl sulfosuccinate for action in the intestine. The gums used for coating herein are polysaccharides which are also broken down by naturally occuring enzymes and absorbed through the intestine.

B. Single or Double Coatings

The coating can be a single coating or multiple coatings. A double coating is preferred. In the preferred double coating, a second coating is selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, sucrose polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, and combinations thereof. Although both coatings are selected from among the same materials, the second coating preferably is different from the first coating; the second coating preferably does not have any appreciable amount of material in common with the first. Each coating can be made up of one or more materials from within the same grouping, eg., a C_{16} triglyceride and a C_{18} triglyceride, and/or between groupings, eg., a C_{16} triglyceride and a pH sensitive polymer. However, it is preferred that a single material be used for each coating.

C. Types of Coating Materials

Preferred coating materials are those which are melted, dissolved, removed or digested in the gastrointestinal tract and which do not appreciably alter the dioctyl sulfosuccinate. Preferred are those coating materials which substantially melt or are

largely dissolved at or about body temperature. The coating material is preferably below the melting point of the dioctyl sulfosuccinate.

Preferred food gums are selected from the group consisting of starches, cellulose derivatives, guar gum, locust bean gum, pectin, algin, carrageenan, xanthan gum, gum arabic, agar, gum ghatti, karaya, tragacanth, and combinations thereof. Some of these are described in Industrial Gums: Polysaccharides and their Derivatives, by R. Whistler and J. BeMiller, Third Edition, incorporated herein by reference (see Chapters 5-8, 13, 18, and 20). Most preferred are cellulose derivatives. Preferred cellulose derivatives are selected from the group consisting of methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxypropyl methylcellulose, hydroxypropyl ethylcellulose, and mixtures thereof.

Preferred C_{14-18} fats herein are trimyristan, tripalmitin, and tristearin. C_{16} and C_{18} fats are preferred. Fats for use herein are preferably solid in the mouth but melt at body temperature. The preferred melting point is between about 95°F and about 99°F. Also preferred are palmitic, oleic, palmitic triglyceride (POP) and soybean hardstock.

Waxes for inclusion with fats herein are esters of long chain fatty acids and long chain alcohols. Preferred are beeswax, and vegetable waxes. More preferred waxes are selected from the group consisting of jojoba, polyethylene glycol of molecular weight between about 1,000 and about 20,000, preferably between about 5,000 and about 10,000, stearin waxes, sorbitan ester waxes, and mixtures thereof. Most preferred is sorbitan tristearin, preferably with soybean hardstock.

C_{16} to C_{20} fatty acids are palmitic, stearic and arachidic. C_{16} and C_{18} fatty acids and sorbitan esters are preferred.

pH sensitive polymers suitable for use herein are selected from the group consisting of cellulose acetate phthalate (CAP), polymethacrylic acid polymers, and mixtures thereof. Eudragit® S-100 for flavored drink mixes and Eudragit® E (Rohm Pharma) for wafers or beverages are most preferred.

Suitable polyol polyesters (called "Olestra") for use herein are described in U.S. Patent 4,005,196, Jandecek et al, issued January 25, 1977, incorporated herein by reference. Sucrose polyester is preferred.

D. Preferred Processes

There are several preferred processes for coating the dioctyl sulfosuccinate. The most preferred process is (a) melting the coating material under a heat within about 10°F, preferably within about 5°F, of the melting point of the coating material, or substantially dissolving the coating material in a solvent, preferably an organic solvent, most preferably acetone, (b) adding the dioctyl sulfosuccinate to a fluid bed

and (c) coating (b) with (a) in the fluid bed. The melted coating material is preferably less than the melting point of the dioctyl sulfosuccinate so that when the dioctyl sulfosuccinate is added, it does not melt. In this way, particles with a core of dioctyl sulfosuccinate surrounded by succeeding layers of coating material are made. This preferred process microencapsulates the dioctyl sulfosuccinate particles, forming larger particles. The fluid bed coating apparatus is preferably a Glatt Powder Coater/Granulator. An even more preferred process is: (a) substantially dissolving the coating material in an organic solvent, (b) adding the dioctyl sulfosuccinate to a fluid bed and (c) coating (b) with the product of (a) in the fluid bed. Most preferably, the dioctyl sulfosuccinate is coated with carboxymethylcellulose and cellulose acetate phthalate. Either one can be the outer coating. Preferably, two successive, different coatings are applied to the dioctyl sulfosuccinate

A second preferred process is (a) melting the coating material under a heat within about 10 °F, preferably within about 5°F, of the melting point of the coating material, and preferably below the melting point of dioctyl sulfosuccinate, (b) adding the dioctyl sulfosuccinate to the product of step (a), and (c) spray congealing or spray quenching the product of (b); wherein the coating material is selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, C_{14-18} fats and waxes, and mixtures thereof. This is believed to be a macroencapsulating process, where particles or flakes of coating material containing smaller particles of dioctyl sulfosuccinate are made. This process involves spray entraining the dioctyl sulfosuccinate in the coating material. It is believed that a matrix of coating material and dioctyl sulfosuccinate is thus formed.

In the more preferred spray congealing process, the product of (b) is preferably sprayed into air, preferably dehumidified, which is at a temperature below the melting point of the coating material, so that solidification into small particles takes place. In the spray quenching step, the product is preferably sprayed , most preferably via nozzle(s), into a liquid, preferably water,. which is at a temperature below the melting point of the coating material The air or liquid is most preferably at a temperature more than about 30°F less, preferably more than about 70°F less, than the melting point of the coating material. The liquid should not be one which would dissolve the particles formed.

A third preferred process is (a) substantially dissolving the coating material in a solvent, preferably an organic solvent. most preferably acetone, (b) adding the dioctyl sulfosuccinate to the product of step (a), and (c) spray drying. Spray drying is preferably into air which has been heated to a temperature at or above the vaporization temperature of the solvent. The solvent should not be one which

dissolves the dioctyl sulfosuccinate. This process involves spray entraining the dioctyl sulfosuccinate in the coating material.

For these processes, the product of step (c) is preferably, in step (d), combined with bulk fiber selected from the group consisting of psyllium, methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, and mixtures thereof. Then, preferably, a drink mix, chewable tablet, or food form is made from the product of step (d), preferably along with other ingredients commonly used in that form. The final composition is preferably within the scope of the composition invention described herein.

The coating herein preferably (1) completely covers the entire surfaces of all dioctyl sulfosuccinate particles, (2) is of sufficient thickness to delay dioctyl sulfosuccinate release during consumption, and (3) will release in the digestive system to provide the dioctyl sulfosuccinate.

Upon completion of the coating process the particles can be tested for leakage of the dioctyl sulfosuccinate. This leakage preferably should not exceed 20 ppm in 240 milliliters of water per 240 milligram dose.

Plasticizers, such as castor oil, triethylcitrate, and acetylated monoglycerides, are optionally and preferably included in the coating solution. The product of step (b) preferably comprises, by weight: from about 70% to about 95%, more preferably from about 80% to about 90%, of solvent; from about 5% to about 20%, more preferably from about 10% to about 15%, of the coating material; and from about 1% to about 10%, more preferably from about 2% to about 5%, of plasticizer. It most preferably consists essentially of 83-87% solvent; 10-13% barrier material; and 2-4% plasticizer.

The coating materials are preferably coated on the dioctyl sulfosuccinate from the product of step (a) to coating ranges of, by weight, from about 1% to about 50%. The coating materials are more preferably coated on the dioctyl sulfosuccinate from, for example, aqueous solutions, organic solvent solutions or hot melts, to coating ranges of, by weight, preferably from about 5% to about 30%, most preferably from 8% to 20%.

One embodiment of this invention is where the dioctyl sulfosuccinate is coated with pH sensitive celluloses or cellulosic films, waxes, fats, gums, methacrylic acid polymers, acetylated monoglycerides, or combinations thereof, and then included in the composition with the bulk fiber. Possible combinations include dioctyl sulfosuccinate coated with an occlusion hydrophobic fat, wax, or gum, then with a pH sensitive material (eg, cellulosic or polyacrylic acid polymer). This

encapsulated form would preferably be mixed with the bulk fiber in a powdered drink mix, chewable tablet, or a food form.

The following examples illustrate the compositions and processes of the present inventions. They are presented by way of example only and are not to be construed as limiting the scope of these inventions.

All parts, percentages, and ratios used herein are by weight unless otherwise specified. All references cited herein are expressly incorporated by reference.

EXAMPLE I

Drink Mix Composition

A composition of the present invention is as follows. This composition is preferably a drink mix used for the treatment of occasional constipation. The drink mix is mixed with at least 8 oz. of liquid and ingested so as to provide the following amounts of psyllium and dioctyl sodium sulfosuccinate.

Component	Amount
Psyllium husk	5.1 grams
Dioctyl sodium sulfosuccinate	240 milligrams

The psyllium husk is milled to a small particle size: no more than 4% on 100 mesh and betwen 25% and 50% through 200 mesh, preferably according to U. S. Patent 5,149,541, Leis, Jr. et al, issued September 22, 1992. These psyllium particles are then agglomerated with maltodextrin and citric acid is sprayed on, preferably according to U. S. Patent 4,459,280, Colliopoulos, issued June 10, 1984 and U. S. Patent 5,219,570, Barbera, issued June 15, 1993.

Dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, can be substituted for the dioctyl sodium sulfosuccinate, or two or three of these can be combined.

Methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, or mixtures of these can be substituted for the psyllium. The amounts of psyllium and/or dioctyl sulfosuccinate can be varied within the ranges specified herein.

EXAMPLE II

Tablet Composition

A composition of the present invention in the form of a tablet is as follows.

Material	Weight %
Methylcellulose	76.3

Dioctyl sodium sulfosuccinate	19.7
Disintegration agent	4.0

These tablets are made by a standard wet granulation process. The tablet target weight is 525 milligrams. The tablet hardness target is 23 SCUs.

Psyllium, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, or mixtures of these can be substituted for the methylcellulose. The amounts of psyllium and/or dioctyl sulfosuccinate can be varied within the ranges specified herein.

Dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, can be substituted for the dioctyl sodium sulfosuccinate, or two or three of these can be combined.

EXAMPLE III

Food Wafer Composition

A composition of the present invention in the form of a wafer food is as follows.

Raw Materials	Weight %
Ascorbic acid	0.15
Natural and artificial flavors	1.54
Corn oil	14.80
Cornstarch	1.97
Fructose crystalline	6.82
Lecithin oil	0.99
Molasses granular light	0.39
Oat hull fiber	6.42
Psyllium husk	13.32
Sodium bicarbonate	0.20
Sucrose white granulated	17.40
Table oats	8.89
Water purified USP	Balance
Wheat flour	19.21
Docusate sodium	0.63
Sorbitan tristearin	0.20

Procedure: In a Hobart bowl add corn oil and lecithin and mix for one minute using speed #1. Note: pre-heat (microwave) lecithin, if necessary. Add psyllium, docusate (which has been coated with the sorbitan tristearin) and mix for one minute using speed #1. Into a separate Hobart bowl, add part of the sucrose, fructose,

molasses and half of the water. Mix for 1 minute using Speed #1. Add psyllium/oil/lecithin pre-mix, and oat-fiber. Mix for 1 minute Add rest of water, soda, flavors, ascorbic acid, and starch. Mix for 1 minute w/speed #1. Add flour to the mixer and mix for 1 minute w/speed #1. Record weight of the entire batch and calculate yield. Roll dough into sheets approximately 0.1 inch thick. Cut dough into rectangles of (about 2.5"L X 1.6"W). Place bars on baking trays and bake at 375° for 10-12 minutes.

Methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, or mixtures of these can be substituted for the psyllium. The amounts of psyllium and/or dioctyl sulfosuccinate can be varied within the ranges specified herein.

Dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, can be substituted for the dioctyl sodium sulfosuccinate, or two or three of these can be combined.

EXAMPLE IV

Tablet Composition

A composition of the present invention in the form of a tablet is as follows.

Raw Materials	% Wt
Psyllium	71.0
Ethylcellulose	4.8
Isopropyl alcohol*	-
Microcrystalline cellulose	16.7
PVP**	1.9
Carnuba wax	2.3
Docusate sodium	3.3

*dried off during drying process

**cross linked polyvinyl pyrollidone

Procedure: Soak ethylcellulose in isopropyl alcohol overnight. Granulate psyllium with isopropyl/ethylcellulose mixture in mixer. Dry at 49°C for 3 hours. Mill through 12 mesh screen. Mix in a mixer the following: psyllium, microcrystalline cellulose and carnuba wax. Compress the tablet per granulation specifications using a tableting press. Coat the core tablets.

Methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, or mixtures of these can be substituted for the psyllium. The amounts of psyllium and/or dioctyl sulfosuccinate can be varied within the ranges specified herein.

Dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, can be substituted for the dioctyl sodium sulfosuccinate, or two or three of these can be combined.

EXAMPLE V

Fat Co-Melt Process

A process according to the present invention is as follows.

Objective:

Coblend dioctyl sodium sulfosuccinate (called docusate sodium), soybean hardstock and sorbitan tristearate in a hot melt, then congeal the blend in cold water and collect the solid particles.

Approach:

Raw Materials: Docusate sodium - 99% pure, SIGMA; dioctyl sulfosuccinate
Sorbitan tristearate - Famodan® TS by Grindsted Products
Soybean hardstock - Durkee Soy I-8

The materials are combined in the following ratios:

	Weight %
Docusate sodium	25.0
Sorbitan tristearate	15.0
Soybean hardstock	60.0
	100.0

These materials are completely melted in a microwave oven. Care is taken to not overheat or scorch the fats. Once melted, the materials are thoroughly mixed. The hot melt is then pumped into a running food processer filled with ice water. The high agitation breaks the melted droplets into small flakes/particles, and the ice water quickly congeals the hot melt. Foaming is likely to occur. The contents of the blender are poured into an 80 mesh sieve and rinsed with cold water. The material is rinsed until no further foaming occurs, which indicates that any docusate remaining on the particles is rinsed away. The resulting particles are fine, irregularly shaped and mostly flakelike in appearance. The particles are air dried.

The experiment can be further refined by varying particle shape, docusate concentration, and types of melted fats. This could reduce surface area thereby reducing the amount of docusate lost during the rinsing step. Surface area may be reduced by changing particle shape and particle size.

EXAMPLE VI

Double Coating Process

A process according to the present invention is as follows.

Objective:

Eliminate the bitter taste of dioctyl sodium sulfosuccinate (called docusate sodium) by applying a double coating.

Coating Material	% Weight	Weight (grams)
Carboxymethylcellulose	5	125
Water *	95	2375

* double distilled, 99.99% pure

Method:

Place 2375 milliliters of the water in a 4 liter beaker. Using mechanical stirring (vigorous--without incorporating air), slowly add 125 grams of carboxymethylcellulose (CMC). It is best to add the powder as a thin stream that will quickly mix into the water without clumping. Addition time for the 125 grams is 10 minutes. Continue stirring for an additional 20 minutes until the solution is clear. If necessary, store at 4°C.

1st Coat Run:

Coating Materials	% Weight	Weight (grams)
Sodium Docusate	29.4	1000
5% CMC Coating Solution	70.6	2400

Method:

Clean and assemble a Glatt Fluid bed coater with Wuester coating chamber. Lift into place. Power up the control panel and start the air turbine. Adjust exhaust flap to 26% and set air inlet temp. to 60°C. Allow to run until inlet air is to set temperature. Stop air and lower assembly. Charge Wuester chamber with 1000 grams of sodium docusate. Chamber partition gap is set at about 1/2 inch. Lift assembly into place and restart air flow. Let run for a few minutes to reach equilibrium and then start pumping the coating solution. Pump at 30 rpm=18 ml/min and an air atomization pressure of 3.2 bar. When run is complete, shut down air and lower assembly. Remove Wuester chamber quickly to avoid contamination of coated product by uncoated powder. Store product in an air tight container at room temperature until next coating step.

2nd Coat Run:

Coating Materials	Weight (grams)
Cellulose acetate phthalate (CAP)	144
Castor Oil	36
Acetone GR	1188
Water *	132

* double distilled, deionized; 99.99% pure

Place 1148 grams of acetone in a 4 liter beaker. With mechanical stirring, slowly add 180 grams of CAP. Stir gently until CAP is in solution. Add 45 grams of castor oil with stirring. Finally, slowly add the water to the solution. A precipitate will form but will redissolve into solution. Reweigh the solution and top off with acetone to 1500 grams to make up for acetone evaporation during mixing. Use 1213 grams of coating solution.

Method:

Clean and assemble Glatt with Wuester coating chamber. Power up control panel and start turbine and heat inlet air to 50°C. Stop air flow and lower assembly, charge Wuester chamber with 970 grams of CMC coated sodium docusate. Raise assembly and restart air. Allow a few minutes to reach equilibrium. Start pumping coating solution. Pump at 150 rpm=46 ml/min, and an air atomization pressure of 2.84 bar. When run is complete, shut down air and lower assembly. Remove Wooster chamber quickly to avoid contamination of double coated product by single coated product. Store finished product in an air tight container.

EXAMPLE VII

Double Coating Process

A process according to the present invention is as follows.

Objective:

Eliminate the negative flavor of dioctyl sodium sulfosuccinate (called docusate sodium) via a double coating, here called barrier (first) and protective (second) coatings.

Approach:

Raw Materials:

(1) sodium docusate (85%) sodium benzoate (15%)

(2) barrier coating
- (a) Eudragit S-100
- (b) Eudragit E
- (c) Cellulose acetate phthalate (CAP)
- (d) Other cellulosic films
- (e) Other pH sensitive films

(3) plasticizers

(a) Castor oil
(b) Triethyl citrate
(c) Acetylated monoglycerides

(Coating Solution: 85% solvent; 12% barrier material; 3% plasticizer)

The sodium docusate is placed in a fluid bed coating apparatus. A solution containing one or more of the barrier coatings named above plus plasticizer is spray coated onto the sodium docusate until it (1) completely covers the entire surfaces of all docusate particles, (2) is of sufficient thickness to delay docusate release during consumption, and (3) will release in the digestive system to provide the dioctyl sulfosuccinate. The coating ranges are expected to be 10 to 25% by weight of the finished coated docusate product.

Upon completion of the coating process the material is tested for leakage. Docusate leakage should not exceed 20 ppm in 240 milliliters of water per 240 milligram dose.

In order to protect the barrier coating during consumption and to provide a means for softening the particles so there is no gritty mouth feel, the coated particles are coated again with a protective coating.

Raw Materials for Protective Coating:

(1) Protective cellulosics
  (A) Methylcellulose
  (B) Carboxymethylcellulose
  (C) Hydroxypropyl methylcellulose

or (2) Protective Waxes/Fats
  (A) Polyethylene glycol
  (B) Sorbitan tristearin/soybean hardstock
  (C) Others

These materials can be coated from aqueous solutions or hotmelts to coating ranges of 8 to 20%.

Other processes of the present invention are obtained when other C_{14-18} fats, C_{16-20} fatty acids, sucrose polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, or combinations thereof are substituted for these coating materials.

Having described the various modifications of the present invention, it will appear to those of ordinary skill in the art that various modifications may be made and that such modifications are intended to be within the scope of this invention.

What is claimed is:

1. A process for making an ingestible, neutral tasting laxative composition by coating dioctyl sulfosuccinate with a material selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, sucrose polyesters, C_{14-18} fats and waxes, pH sensitive polymers, food gums, and combinations thereof.

2. The process according to Claim 1 comprising the steps of: (a) melting the coating material under a heat within -12.2°C (10°F) of the melting point of the coating material, or substantially dissolving the coating material in a solvent, (b) adding the dioctyl sulfosuccinate to a fluid bed and (c) coating (b) with the product of (a) in the fluid bed.

3. The process according to any of the preceding claims wherein two successive, different coatings are applied to the dioctyl sulfosuccinate, preferably first carboxymethylcellulose and then cellulose acetate phthalate.

4. The process according to any of the preceding claims comprising the steps of: (a) substantially dissolving the coating material in an organic solvent, (b) adding the dioctyl sulfosuccinate to a fluid bed, and (c) coating (b) with the product of (a) in the fluid bed in the fluid bed.

5. The process according to any of the preceding claims comprising the steps of: (a) melting the coating material under a heat within -12.2°C (10°F) of the melting point of the coating material, (b) adding the dioctyl sulfosuccinate to the product of step (a), and (c) spray congealing or spray quenching the product of (b); wherein the coating material is selected from the group consisting of C_{14-18} fats, C_{16-20} fatty acids, C_{14-18} fats and waxes, and mixtures thereof.

6. The process according to any of the preceding claims wherein the coating material comprises a C_{14-18} fat selected from the group consisting of trimyristan, tripalmitin, and tristearin.

7. The process according to any of the preceding claims comprising the steps of: (a) melting the coating material under a heat within -15°C (5°F) of the melting point of the coating material, and below the melting point of dioctyl

sulfosuccinate, (b) adding the dioctyl sulfosuccinate to the product of step (a), and (c) spray congealing or spray quenching the product of (b).

8. The process according to any of the preceding claims wherein step (c) is spray congealing, and wherein, in step (c), the product of (b) is sprayed into air which is at a temperature below the melting point of the coating material.

9. The process according to any of the preceding claims wherein step (c) is spray quenching, and wherein, in step (c), the product of (b) is sprayed into a liquid which is at a temperature below the melting point of the coating material.

10. The process according to any of the preceding claims wherein the liquid in step (c) is water which is at a temperature more than -1.1°C (30°F) less than the melting point of the coating material.

11. The process according to any of the preceding claims comprising the steps of: (a) substantially dissolving the coating material in a solvent, (b) adding the dioctyl sulfosuccinate to the product of step (a), and (c) spray drying.

12. The process according to any of the preceding claims wherein the solvent in step (a) is acetone and wherein step (c) spray drying is into air which has been heated to a temperature at or above the vaporization temperature of acetone.

13. The process according to any of the preceding claims wherein the dioctyl sulfosuccinate in the composition is selected from the group consisting of dioctyl sodium sulfosuccinate, dioctyl calcium sulfosuccinate, dioctyl potassium sulfosuccinate, and mixtures thereof.

14. The process according to any of the preceding claims wherein the product of step (c) is, in step(d), combined with bulk fiber selected from the group consisting of psyllium husk, methylcellulose, polycarbophil, calcium polycarbophil, bran, malt soup extract, karaya, guar gum, and mixtures thereof.

15. The process according to any of the preceding claims wherein a drink mix, chewable tablet, or food form is made from the product of step (d).

16. The process according to any of the preceding claims wherein the product of step (b) comprises, by weight: from 70% to 95% of the solvent; from 5% to 20% of the coating material; and from 1% to 10% of plasticizer.

17. The process according to any of the preceding claims wherein the coating materials are coated on the dioctyl sulfosuccinate from the product of step (a) to coating ranges of, by weight, from 1% to 50%.

18. The process according to any of the preceding claims wherein the coating material comprises a food gum selected from the group consisting of starches, cellulose derivatives, guar gum, locust bean gum, pectin, algin, carrageenan, xanthan gum, gum arabic, agar, gum ghatti, karaya, tragacanth, and combinations thereof; a cellulose derivative selected from the group consisting of methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxypropyl methylcellulose, hydroxypropyl ethylcellulose, and mixtures thereof; or a wax selected from the group consisting of jojoba, polyethylene glycol of molecular weight between 1,000 and 20,000, stearin waxes, sorbitan ester waxes, and mixtures thereof; and/or a pH sensitive polymer selected from the group consisting of cellulose acetate phthalate, polymethacrylic acid polymer, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 94/14259

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K9/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 11001 (SOLVAY) 9 July 1992 see claims 1,11,22,23,26,32-34 see page 6, line 4 - page 7, line 14 see page 8, line 9 - line 21	1,13,18
A	EP,A,0 573 978 (KAO CORPORATION) 15 December 1993 see page 4, line 2 - page 5, line 12	3
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 072 (C-570) 17 February 1989 & JP,A,63 264 534 (KAO CORP.) 1 November 1988 see abstract	14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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(54) Title: DOUBLE ENCAPSULATION PROCESS AND FLAVORANT COMPOSITIONS PREPARED THEREBY

(57) Abstract

A flavorant composition which exhibit controlled release properties may be conveniently and economically prepared by a process involving (i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid; (ii) adding an edible solute to the first suspension, to obtain a second suspension, in an amount such that the content of the edible solute in the second suspension is 5 to 55 wt.% based on the total weight of the second suspension; and (iii) subjecting the second suspension to spray drying to obtain the flavorant.

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TITLE OF THE INVENTION

DOUBLE ENCAPSULATION PROCESS AND FLAVORANT COMPOSITIONS PREPARED THEREBY

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a process for producing encapsulated flavor systems which exist in the form of a coacervated flavor core microencapsulated in a spray-dried particle matrix. The present invention also relates to flavorant compositions produced by such a process. The present invention further relates to a new method of coacervation and the products produced by such a method.

Discussion of the Background:

Commercial encapsulation of flavoring materials is generally limited to spray drying and melt extrusion. Flavor encapsulation employing the spray drying process requires that the flavor, in the form of an aqueous emulsion with solubilized carrier solids, be fed into the spray dryer, atomized and dispersed into a heated air chamber plenum, dried, and collected. The resulting product is obtained as a fine particulate with lipid flavor droplets dispersed within the porous particle matrix. The carrier solutes used in the emulsion preparation are required not only to have emulsifying properties but also be bland, exhibit a high degree

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of solubility with low intrinsic viscosity, be non-reactive with the flavor load while retaining volatile components, and exhibit stable powder properties once dried. In almost all commercial production formulas the carrier solutes of choice are usually selected for their emulsifying functionality and high degree of solubility.

It is well known by those skilled in spray drying processes that retention of volatiles is improved with increased dissolved solids levels in the aqueous phase of the emulsion. This requirement generally restricts spray drying encapsulation formulations to the use of highly water-soluble, modified starches, such as the octylsuccinate-derivativized modified starches, or gum arabic as the emulsifying, film-forming carrier polymer component. Soluble, inert carrier components such as sugars, corn syrup solids and maltodextrins are added to the aqueous flavor emulsion in order to increase solids levels, lower ingredient costs, increase yield, and improve product stability.

The spray drying encapsulation process is relatively simple, economical, and easily scaled to large production volumes. A major benefit of spray drying encapsulation relates to the broad range of flavors and flavoring systems which can be prepared. These flavorings include oil-soluble flavors, water-soluble compounds, natural extracts, single component flavor compounds, as well as complex compounded flavors having both water- and oil-soluble components.

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The spray drying of flavors is well described in the art. G. Reneccius describes the control of a number of the process and carrier composition variables which lead to improved yields for the spray drying of orange oils, while also improving the stability of citrus terpenes to oxidation in the resulting product (see: Flavor Encapsulation, American Chemical Society Symposium Series #370, S. Risch and G. Reneccius, Eds. 1988, Chapter 7, which is incorporated herein by reference.). Among the key parameters identified are choice of emulsifying carrier, dissolved carrier solids levels, and control of inlet and outlet air temperatures within the drying chamber.

U.S. Patent No. 3,971,852 discloses the encapsulation of very high levels of an oil flavor in selected matrix compositions by spray drying. This patent discloses specific binary carrier compositions consisting of a polymer and polyol or sugar which allow the droplet matrix to retain its continuous, plastic film character during the initial drying stage, ultimately yielding particles characterized as having a glassy character and reduced porosity. Claims for high oil loads of up to 80% by volume as well as low levels of surface oil are made.

U.S. Patent No. 4,532,145 describes use of a binary spray drying carrier composition consisting of a low molecular weight component 90-500 Daltons (10-30%), and a higher molecular weight component 1000-6000 Daltons (70-90%) which are combined in

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solution and employed as the carrier encapsulating media for spray drying and stabilization of volatile flavorings.

U.S. Patent No. 5,124,162 teaches the fixation of flavors by spray drying with a carrier composed of mono- or disaccharides (22-45%), maltodextrin (25-50%), and a film-forming polymer (10-35%). A densified particle is obtained having a free flow bulk density of at least 0.50 g/cc with less than 20% voids in the particle.

U.S. Patent No. 5,087,461 teaches an encapsulation process consisting of an initial spray drying of a volatile flavor followed by melt extrusion of the spray-dried flavor in a carbohydrate matrix. The matrix composition consists of a chemically modified starch (40-80%), a maltodextrin (10-40%), corn syrup solids or polydextrose (5-20%), and mono- or disaccharide (5-20%) and flavor to obtain a solid, glassy encapsulation matrix.

While commercial spray drying encapsulation accounts for the vast majority of manufactured encapsulated flavors, one key limitation of these products is the lack of any controlled release functionality.

Coacervation encapsulation, a technology commercialized in the 1950s, yields true controlled release functionality and has found wide usage in the pharmaceutical, fragrance and specialty products industries. However the relatively high process costs, sensitive multi-step batch process, regulations limiting the

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number of polymeric agents which can be used in food preparations, and the difficulty in dealing with encapsulates having both aqueous and lipid solubility properties has drastically limited the application of coacervation for flavor encapsulation in the food industry. A general discussion of these issues is provided by R. Versic in Flavor Encapsulation, American Chemical Society Symposium Series #370, S. Risch and G. Reneccius, Eds., 1988, Chapter 14, "Coacervation for Flavor Encapsulation," which is incorporated herein by reference.

Coacervation microcapsule systems can be generated in the form of simple coacervates, which are derived from a single polymer species in solution. Complex coacervates, which require the interaction of two distinct and oppositely charged polymer species, are also well characterized.

The coacervation process for flavor encapsulation consists of the following general steps: (1) dissolution of the polymer(s) at predetermined concentration(s) in aqueous solution(s); (2) emulsification of the flavor oil in the aqueous solution (and addition of the second polymer in the case of complex coacervation); (3) coacervation or phase separation of the polymer(s) by means of a change in temperature, pH, or dilution, or by addition of a water-miscible co-solvent or salt to generate a controlled phase separation with the concomitant association of the enriched polymer phase around the flavor oil droplet; (4) optionally chemically cross-linking the hydrated coacervated

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polymer phase ; (5) decanting the liquid media and washing the retained microencapsulated product free of undesirable solutes; and (6) optionally drying the recovered capsules.

The coacervation microencapsulation process has not been significantly applied in the flavor encapsulation field for a number of practical reasons. First, only water-insoluble flavorings can be easily encapsulated when utilizing an aqueous medium for polymer solubilization and flavor emulsification. This limitation results from the fact that the water-soluble flavor components will partition into the aqueous phase, not only changing the flavor profile of the retained encapsulated flavor oil but also interfering with interfacial surface tension dynamics involved in formation of the coacervating polymer layer around the flavor droplet. Secondly, the requirement of generating dilute polymer solutions with complex coacervation leads to handling large volumes of liquid media in a batch operation. Thirdly, the sensitive nature of the complex coacervation process can lead to scaling problems when attempting to go from laboratory to production volumes. While these limitations are well known in the coacervation encapsulation field, the ability of coacervation encapsulation to exhibit true controlled release properties in response to moisture, heat, and mechanical stress makes it a desirable encapsulation technology.

Issues relating to the commercial scale-up of microencapsulation processes have been reviewed in some detail by

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V.A. Crainich, Jr. in "Microencapsulation: Scale-up Considerations and Production Technology", Drugs and Pharmaceutical Science, Volume 41, pp. 221-255 (1990), which is incorporated herein by reference. The drying of microcapsules is discussed. It is stated that a combination of drying systems is usually necessary to obtain dry, free-flowing microcapsules. Commercial drying systems that have been employed for this purpose include spray dryers, tower dryers, fluid-bed dryers, flash dryers, tray dryers, and rotary dryers in both batch and continuous configurations. Chemical agents utilized in the treatment of wet microcapsules before drying include the addition of surfactants, or drying aids such as silicates, talc, and starches which are employed as part of a combined system. The disclosed preferred system for drying microcapsules is the batch, fluidized bed dryer employing drying aids (pages 249-51 of the above reference.)

U.S. Patent No. 3,647,481 mentions coacervation encapsulation in relation to a series of aliphatic di- and tri-sulfides as flavoring compositions. In one Example, a flavor composition is encapsulated by complex coacervation and capsules obtained by spray drying. No disclosure of the spray drying process conditions or the use of carriers is given.

Preparation and compositions of coacervated encapsulated flavor oil capsules are disclosed in International Patent Application WO 93/19621. Flavor oils are microencapsulated by

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coacervation, cross-linked, and partially dewatered. International Patent Application WO 93/19622 discloses the preparation of heat-stable, fracturable, spray-dried oil microcapsules. The wet coacervate capsules are washed and dispersed in water to form a slurry, silicon dioxide is added as an anticaking agent, and the dispersed system is spray dried.

A coacervate consisting of a non-polar wall forming polymer and a polyelectrolyte polymer for encapsulation of a core material is disclosed in U.K. 1,071,169. Solutions of the non-polar polymer, such as methylcellulose, and the polyelectrolyte, such as sodium carboxymethylcellulose or gum arabic, are treated with ammonium or sodium sulfate, coacervation is initiated, and capsules are collected and dried in a hot air stream. No spray drying or addition of drying carriers is taught.

H. Takenaka, Y. Kawashima, and S.Y. Lin, in J. Pharmaceutical Sciences, Volume 69, No. 5, pp. 513-516 (1980), describe a study in which gelatin-gum acacia coacervate microcapsules containing sulfamethoxazole were prepared. Experimental drying procedures describe both solvent dehydration and spray drying of the coacervate. Spray drying was performed by suspending the coacervate microcapsules in distilled water and pumping the water-coacervate slurry into the spray drier.

U.S. Patent No. 3,872,024 discloses the use of inorganic polymeric solutes to induce liquid-liquid phase separation of water-soluble polymers. A sodium polyphosphate solution is mixed

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with a gelatin solution at elevated temperatures, the pH is adjusted to 6.8, and the polymer-inorganic polymer interactions are initiated. An encapsulant liquid is added, and the solution is allowed to slowly cool to develop the coacervate at room temperature. The system can then be cooled to 5°C to harden the gelatin microcapsule wall which is crosslinked with glutaraldehyde. Capsules are collected by filtration, washed, and dried by conventional means. There is a brief reference to hot air drying of the recovered capsules but no details are provided.

U.S. Patent No. 3,567,650 discloses the use of aqueous solutions of methylcellulose as the wall forming polymer in a coacervation process. The methylcellulose, in the presence of a complimentary hydrophilic polymer such as dextran, polyvinylpyrrolidine, polyvinylalcohol or gum arabic, forms the coacervate encapsulate with a variety of materials including lemon oil, aspirin, menthol and various drugs. In the disclosed preferred embodiment, the polydispersed aqueous coacervate system is brought to 50-60°C inducing wall formation by the methylcellulose to assist in recovery of the microcapsule. After removing excess water at the noted elevated temperatures, the microcapsules were dried using conventional techniques.

Thus, it is clear that flavorant compositions obtained by both spray drying and coacervation, although each offering advantages to the food industry suffer from notable drawbacks.

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Accordingly, there is a need for flavorant compositions which are free from such drawbacks. Additionally there is a need for a process to generate such encapsulated flavors. There also remains a need for new methods to effect coacervation.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel flavorant compositions.

It is another object of the present invention to provide novel flavorant compositions which are economical to prepare.

It is another object of the present invention to provide novel flavorant compositions which exhibit controlled release properties.

It is another object of the present invention to provide novel flavor compositions which are in the glassy state.

It is another object of the present invention to provide a process for preparing such flavorant compositions.

It is another object of the present invention to provide a process for preparing such flavorant compositions which is economical carry out.

It is another object of the present invention to provide a new method of encapsulating a flavor by coacervation.

These and other objects which will become apparent during the following detailed description have been achieved by the

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inventor's discovery that such flavorant compositions may be prepared by a process comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid;

(ii) adding an edible solute to the first suspension, to obtain a second suspension, in an amount such that the content of said total edible solute in said second suspension is 5 to 55 wt.%, based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

Figure 1 is a photomicrograph of a coacervate of orange oil prepared by utilizing a hydroxypropylmethylcellulose maltodextrin system. The coacervate was diluted in additional 35% maltodextrin solution to show the botryoid form as prepared in Example 1 (at 400x magnification); and

Figure 2 is a photomicrograph of the double encapsulation product of Example 1 (xylene mount at 200x magnification).

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present process involves first preparing a coacervated flavor microcapsule in a liquid medium. The flavor can be a compounded oil flavor, an essential oil, an oleoresin, an ampiphatic flavor dissolved in or diluted in a lipophilic flavor solvent such as triacetin, medium chain triglycerides or vegetable oil, or a natural flavor extract which contains water-soluble components. Specific examples of preferred flavoring agents include essential oils such as the citrus oils (lemon, lime, orange, tangerine), anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil; spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; allium oils (onion, garlic, chive), butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols, ketones, esters, aldehydes and fatty acids, as well as oil extracts of reaction flavors, fruits and vegetables.

The flavor is emulsified in an aqueous polymer solution to obtain dispersed flavor droplets. The coacervating water-soluble polymer can be chosen from the group of food grade materials including gelatin, gum arabic (acacia), methylcellulose, hydroxypropylcellulose, propylene glycol alginate, hydroxypropylmethylcellulose, sodium carboxymethylcellulose,

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sodium alginate, xanthan gum, gum tragacanth, locust bean gum, carageenan(s), modified food starch(s), sodium polyphosphates, low methoxy pectin, pectin, and other water soluble food polymers as noted by R. Versic in Flavor Encapsulation, S. Risch and G. Reneccius, Eds. ACS Symposium Series #370, (1988) Washington, D.C., pg. 130, which is incorporated herein by reference.

The coacervation process may be carried as described in C. Thies in Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley and Sons, Inc., New York, vol. 9, pp. 724-731 (1987) and in C. Thies, "Physiochemical Aspects of Microencapsulation," in Polymer-Plastic Technology and Engineering, vol. 5(1), pp. 1-22 (1975), and in U.S. Patent Nos. 2,800,457, 2,969,331, 3,043,782, and 3,567,650, all of which are incorporated herein by reference.

Typically, the flavoring agent in a simple coacervate system is dispersed in the warm aqueous polymer solution in an amount of 1 to 20 wt.%, preferably 5 to 15 wt.%, based on the total weight of the original initial aqueous solution.

A simple coacervate may utilize a hydrophilic polymer such as gelatin. For this coacervate system, a 5 to 15 wt.% gelatin solution is prepared and held at a temperature above 40°C. Following the emulsification of the flavoring in the heated gelatin solution, a phase separation inducing agent is added, and the mixture is agitated at the desired temperature until the coacervation is complete. To those skilled in the art, it is

well known which specific coacervating or phase separation inducing agents may be employed for simple coacervates of water-soluble polymers. The use of water-miscible solvents such as ethanol, isopropanol, and acetone are well characterized. Salting out agents such as sodium sulfate and sodium polyphosphate are also routinely used. (see Theory and Practice of Industrial Pharmacy, L. Lachman, H. Lea and J. Kanig, Eds., pgs. 412-429, Lea and Feiberger, Philadelphia, 1988, which is incorporated herein by reference).

For preparation of complex coacervates, the preferred systems are gelatin-gum arabic, gelatin-sodium alginate, or gelatin-sodium polyphosphate. In the case of gelatin-gum arabic complex coacervate systems, the concentration of the initial gelatin polymer solution is generally 1.4 - 15 wt.%, and, similarly, the concentration of the initial gum arabic polymer solution is generally 1.4 to 15 wt.%. Following the emulsification and combination steps, the gelatin-gum arabic solution is diluted to a preferred final concentration of 1.2 to 2.5 wt.% for each polymer. The gum arabic solution is generally used to emulsify the flavor oil. The flavor oil is utilized in an amount such that the ratio of oil to polymer is from 1:1 to 100:1. Then the gelatin polymer solution is added to the emulsion while the temperature of the solution is initially maintained above the gelation temperature of the gelatin (40 to 50°C). The gelatin and gum arabic solutions are combined in an

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amount such that the weight ratio of gum arabic to gelatin is 1.5:1 to 1:1.5, preferably about 1:1. The pH is then adjusted to 3.8-4.3 with dilute acid. The mixture is diluted with distilled water to yield a final solution concentration of 1.0 to 2.5 wt.% and cooled slowly to ambient temperate and maintained. Following formation of the complex coacervate shell around the flavor droplet, the solution can be brought to 5-10°C and a cross-linking agent such as glutaraldehyde added to insolubilize the core wall.

Although the coacervated microcapsules may be separated and washed prior to mixing with the edible solute, the spray drying of the coacervate can be made more efficient and result in increased recovery of the microcapsules if the edible solute is added to the original microcapsule suspension. The choice of edible solute material must meet the general criteria of exhibiting good water solubility, extremely bland taste, yield free-flowing and non-caking powder in the dried form, be non-crystallizing, and be non-reactive to the microcapsule shell and flavor components. The edible solutes which meet all the criteria include: maltodextrins 5-15 DE, corn syrup solids 20-42 DE, modified corn starches (n-octylsuccinate modified starch), sodium hexametaphosphates, sodium polyphosphates, citric acid-sodium citrate (binary mixtures), hydrolyzed gelatin, polydextrose and mono- and disaccharides. Other soluble, functional food polymers which may optionally be added as

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minority components to the bulk carrier solutions as cosolutes, where compatible, include proteins such as gelatins(s), dairy proteins and isolates such as casein, whey proteins, and lactoalbumins; soy proteins, corn proteins; modified celluloses such as methylcellulose, hydroxypropylmethyl cellulose, carboxymethylcellulose, and hydroxypropylcellulose, gums and hydrocolloids such as xanthan, guar, locust bean, acacia carrageenan(s), alginate(s) and pectin(s) among others. In choosing the solute system, the primary criteria will be ease of solubility and stable powder properties. In many instances, compatible mixtures of soluble components may be utilized. Other applications will dictate the choice of edible solutes. When using sodium polyphosphates, it is preferred to use a maltodextrin in approximately equal levels to assist in retaining a free-flowing powder. When employing octylsuccinate modified starch, the use of the sodium citrate or citric acid-sodium citrate mixtures as the neutralizing agent to reduce the normally acidic character of the dissolved solids media is preferred.

In complex coacervation systems, the use of citric acid-sodium citrate buffer as a pH adjusting agent yields an additional advantage to the process. Additional edible solute materials can be then chosen from the materials cited above.

The use of hydrolyzed gelatin as an edible solute component may be employed where glutaraldehyde has been used for the crosslinking of the coacervate shell wall. Addition of 2-20 wt.%

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of hydrolyzed gelatin to the dissolved solid will react with any unreacted glutaraldehyde remaining in the aqueous solution.

Typically the edible solute is added to the first suspension containing the coacervated microcapsules in an amount of 5.0 to 55 wt.%, preferably 20 to 45 wt.%, based upon the total weight of suspension including flavor oil and microcapsule wall.

When utilizing the double encapsulation process, citrus oils, spice oils and oleoresins are easily processed as the flavor encapsulate. Following coacervation and crosslinking, the microcapsules can be decanted, washed with distilled water, and resuspended in a pre-prepared solution of edible solute. Alternatively, when the core flavoring system contains limited quantities of water-soluble components, a partitioning response will occur during the emulsification step as the water-soluble components migrate into the aqueous phase from the dispersed lipid droplets. In these cases, the original aqueous medium used in the coacervation step can be retained with its soluble flavor components. Then the addition of solid edible solutes to the original encapsulation solution is preferred. An added benefit accrues to the spray drying step with the added low-molecular weight solids which increase retention of the water soluble volatiles. Proper selection of the added low-molecular weight solid can yield a matrix in the glassy state further enhancing long term retention of the volatile water-solubilized flavoring components.

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In another embodiment, lipid-soluble flavor fixatives such as waxes and ethylcellulose can be combined with the lipid encapsulant before the emulsification step to retard flavor transport to the aqueous phase and improve flavor release in the final applications. The use of oil densifying agents such as brominated vegetable oils or ester gums, employed in the densification of the drink oil flavorants, can also be added to the flavor oil before coacervation step.

After the addition of the edible solute, the mixture is then spray dried. Any conventional spray drying apparatus may be used.

The addition of the edible solutes to the coacervated microcapsule aqueous suspension will increase the density of the aqueous phase. This can result in a "creaming" of the microcapsules prepared from lower density oils. While continuous agitation will redisperse the flocculated layer, low shear pumping of the aqueous suspension through extended lengths of the tubing leading to spray drier nozzle can lead to reflocculation, separation and disproportionation within the feed stream. To counter this effect, it is recommended that the coacervate fluid reservoir be placed in close proximity to the spray drier nozzle inlet. The use of in-line mixers and reduced tubing diameters to increase fluid shear will ameliorate separation of the microcapsules during pumping. Other atomizing nozzle and spray

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drying systems such as used for the spray drying of cheese or hydrolyzed vegetable powders may also be employed.

The breadth of applications of this microencapsulation technology can be expanded into many other areas. For example, in the encapsulation of savory flavors, salt would normally be used as a flavor enhancer. In those cases, sodium and potassium chloride may be employed as one of the coacervation-inducing solutes and be retained in the second suspension, and ultimately, the spray dried product.

In the pharmaceutical industry, the need for additional controlled release microencapsulation systems could easily make use of this double encapsulation process with water-insoluble bioactive agents, or pharmaceutical materials which can be dissolved oil. Methylcellulose and hydroxypropylmethylcelluloses have been extensively employed as a hydration-retarding, control release agent in tablet formulations. With the double encapsulation product the methylcellulose and hydroxypropylmethylcellulose coacervate can be prepared, surrounding the discrete pharmaceutical agents and extending the control release functionality in standard tableting formulations. Other additional benefits of the double encapsulation process using the methylcellulose-maltodextrin simple coacervate system would include the increase in recovery of extremely expensive pharmacological materials, in addition to the ability to produce

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homogeneous amorphous or glassy powders under sterile drying conditions.

In another embodiment, the present invention provides a simple coacervate system based upon a specific coacervation response of methylcellulose or hydroxypropylmethylcellulose polymer solutions. These polymer solutions have been found to form a coacervate upon addition of specific soluble, edible, carbohydrate oligomers. These carbohydrate oligomers are characterized as having Dextrose Equivalents of D.E. 2-42, which correspond to the maltodextrins (D.E. 1-15) and to corn syrup solids (D.E. 20 -42). The coacervation of the methylcellulose (and hydroxypropylmethylcellulose) is believed to result from interactions with the carbohydrate oligomers, i.e. the Dobry effect.

The flavor oil, in ratios of 0.5 to 80 parts flavor oil to one part polymer, is emulsified in the surface-active methylcellulose polymer solution made up as 0.5 to 6.0 wt.% polymer at ambient temperature. A carbohydrate co-solute, preferably maltodextrin or in a more limited instance corn syrup solids, is added slowly preferably in the solid form with continuous stirring until a phase separation is induced. In an alternative embodiment, a concentrated solution of maltodextrin (30-55 wt.%) can be slowly added with continuous stirring. Using a 10 D.E. maltodextrin, this phase separation is observed at approximately 18 wt.% added maltodextrin with methylcellulose (or

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hydroxypropylmethylcellulose) present at a concentration of 2 wt.% in the original polymer solution.

The methylcellulose or hydroxypropylmethylcellulose can be of various substitution character and viscosity grades. These materials are commercially available from the Dow Chemical Company as the product Methocel®, in the form of methylcellulose (A series) or hydroxypropylmethylcellulose (E, F, J, K series) which are comprised of varying molecular weights and are referenced in terms of their solution viscosities. The upper practical concentration of the Methocel® material is determined by the limiting intrinsic viscosity of the polymer solution for practical emulsification of the flavor oil.

The response of methylcellulose solutions to the presence of other dissolved solutes is discussed briefly in the Dow Chemical Company Technical Handbook "METHOCEL Cellulose Ethers." In this technical brief, the tolerance of aqueous solutions of Methocel® to salts and sugar are noted at specific levels. With 100 ml of an aqueous 2% solution of the various Methocel® materials, 65 to 120 grams of sucrose will cause the polymers to phase separate. This response is explained in terms of the high concentration of the sugar solute competing for the water required to solvate and keep the polymer in a hydrated state. The concentrations of added electrolyte salts required to salt out the hydrated methylcellulose polymers under similar experimental conditions are also described. Maltodextrins with their larger average

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molecular weights exhibit phase separation inducing responses at much lower concentration levels and are more likely to be polymer-polymer interactions.

The methylcellulose or hydroxypropylmethylcellulose flavor coacervate is characterized as a dispersion containing individual droplets of flavor surrounded by the enriched polymer phase as well as botryoid clumps of the encapsulated flavor oil droplets. The coacervated droplets prepared in Example 1 are shown as formed in the aqueous phase in Figure 1.

After the coacervation step is complete, addition of a water-soluble carrier solute will improve spray drying yield and drying efficiency in the production of the double encapsulation product. The dried particles are obtained in the form of a carrier matrix with interdispersed flavor droplets surrounded by a concentrated methylcellulose coacervate film. Figure 2 is a photomicrograph of the spray-dried double encapsulated coacervate as prepared in Example 1.

The polymer-polymer interactive response of other water-soluble, hydrophilic food polymers in solution with maltodextrin were evaluated. Solutions of modified cellulose such as carboxymethylcellulose of varying viscosities; gums and hydrocolloids such as guar, locust bean, xanthan, sodium alginate, algin, propyleneglycol alginate, pectin, low methoxy pectin, tragacanth, arabic; n-octylsuccinnalated starch, and gelatin were prepared at 1 wt.% or 2% levels. Then maltodextrin

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was added reaching 20 wt.% and 30 wt.% levels in the presence of the prehydrated aqueous polymers. Only gelatin showed a limited phase change response. None of the other above-listed polymers interacted with the equivalent or higher concentrations of maltodextrin.

Other solutes that have been found to generate a coacervate with the methylcellulose polymers are the sodium (or potassium) polyphosphates. Suitable polyphosphates include sodium polyphosphate, glassy, sodium or potassium tripolyphosphate, and sodium hexametaphosphate (commercial source FMC). The mechanism involved is the classical salting out response as noted above which has been employed for coacervation with a number of water-soluble polymers as disclosed in U.S. Patent No. 3,872,024, or U.S. Patent No. 2,800,458 and in U.K. 1,071,169.

In the double encapsulation embodiment where the initial coacervation step utilizes a polyphosphate solute, maltodextrin is added to the microcapsule-phosphate dispersion to obtain a free-flowing, stable spray dried product. The use of polyphosphate alone followed by spray drying of dispersed capsules in the polyphosphate solution will result in the capsules sticking to the spray dryer chamber walls and severe losses of product.

In an alternative embodiment, a mixture of maltodextrin-sodium polyphosphate powder is preblended and added as the coacervation inducing solute. The preferred ratio of the mixture

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being ≥ 1:1 maltodextrin:polyphosphate. The resulting spray dried coacervate powder product will be obtained as a stable free-flowing powder.

In most drying processes involving complex coacervation microcapsules, the microcapsules are separated from the original process solution, washed and suspended in water, silicon dioxide optionally added, and the capsules dried in a fluidized bed drier. The present double encapsulation process will work equally well with the complex coacervate systems. For those cases, the recovered capsules can be crosslinked, washed, suspended in 30-40 wt.%, dried solids basis (dsb) maltodextrin solution and spray dried. Alternatively the original reaction solution can be retained, carrier solids added, and the system spray dried.

For formation of the simple methylcellulose coacervate, the preferred carbohydrate co-solute, e.g. the maltodextrin, functions not only as the coacervate inducing oligomer but also as a spray drying process aid. This use results in increased recovery of the microcapsules, and a free flowing, non-caking powder product. The final total solid of the second suspension system for spray drying is typically in the range of 30-50 wt.%. Following addition of the maltodextrin and coacervation, other selected solids can be added to increase dissolved solids levels of the solution preceding the spray drying. These additional solute materials must meet the general criteria of exhibiting

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high water solubility and low intrinsic viscosity, being extremely bland, being non-reactive to the microcapsule shell and flavor core, as well as yielding free-flowing, non-caking and non-crystallizing powders in the dried form. Edible solute materials and mixtures thereof which meet all these criteria include corn, potato and tapioca derived maltodextrins (5-15 D.E.), other dextrins, corn syrup solids (20-42 D.E.), modified corn starches (n-octylsuccinate modified starch), sodium hexametaphosphates, sodium polyphosphates, citric acid-sodium citrate (binary mixtures), polyols such as mannitol, lactitol and sorbitol, polydextrose, hydrolyzed gelatin, and mono- and disaccharides individually and as mixtures. In many instances, compatible mixtures of lower molecular weight carbohydrates such as corn syrup solids and maltose will be added to the maltodextrin solution when formation of a glassy state is desired with the spray dried product. Other soluble food polymers which may be added as minority components to the bulk carrier solutions as co-solutes, where compatible, include proteins such as gelatins, dairy proteins and isolates such as casein, whey proteins, and lactoalbumins; soy proteins, corn proteins; low viscosity gums and hydrocolloids. When employing the octylsuccinate modified starch, the use of sodium citrate or citric acid-sodium citrate mixtures as a neutralizing and buffering agent to reduce the acidic character of the dissolved solids media is preferred.

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Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

Example 1.

A simple coacervate was prepared as follows: a 2.0 liter solution of 4.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel E15) is prepared at ambient temperature and 100 grams of an orange oil (Citrus and Allied, single fold) is emulsified by slow addition to the polymer solution using an Arde-Barinco laboratory homogenizer at a low power setting. Following emulsification of the orange oil, 700 grams of 10 D.E. maltodextrin solids (American Maize, Lodex-10) are added slowly with continuous agitation over a 30 minute period. At approximately 20% added maltodextrin (total solids basis), a phase change is noted as the initial formation of a flocculated dispersion. The remaining maltodextrin is slowly added until the total final level of 35 wt.% (total solids basis) is reached. The orange oil suspension is stirred gently at ambient temperature to keep the coacervate from "creaming" for an additional hour. Then the orange oil coacervate dispersion in the maltodextrin solution is fed into a pilot plant Niro spray drier set with the inlet air temperature set at 390°F and outlet

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temperature of 201°F at a rate of 2.5 lbs/hr and spray drying completed. Total solids recovered are 60% based upon components (oil-methylcellulose-maltodextrin) of the system. The product is obtained as a free-flowing amorphous powder with a particle density of 1.15 g/cc.

Example 2.

A coacervate was prepared as follows: A 1.0 liter solution of 6.0 wt.% methylcellulose (Dow Chemical, Methocel A15LV) was prepared and held at ambient temperatures. Then 73 grams of a compounded garlic flavor oil was slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer set at low power. Following the emulsification, 600 grams of a 1:1 dry blend mixture maltodextrin:sodium hexametaphosphate was slowly added with continuous stirring over a period of 30 minutes. During addition of the solids, a phase change is noted. The coacervated flavor is held with continuous stirring for an additional 2 hours. The suspension of the coacervated garlic oil is continually stirred and fed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 380°F and outlet temperature of 199°F. The double encapsulated product was obtained as a free-flowing powder. DSC analysis shows the powder to be in a glassy state with a Tg of 48°C.

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Example 3.

A coacervate was prepared as follows: A 1.0 liter solution of 2.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel F50) was prepared and held at 23°C. Then 72.6 grams of a compounded oil-soluble butter flavor containing approximately 20% of a water soluble flavoring component, diacetyl, is slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer. After the emulsion has been prepared, the pale yellow color of the diacetyl is observed in the aqueous phase. Then 422 grams of solid maltodextrin (Lodex-10, American Maize Co.) was added slowly with continuous stirring. With the addition of approximately 200 grams of the total 422 grams maltodextrin, a phase change is noted as a flocculated oil phase. Then additional solute consisting of 211 grams of a mixture of citric acid-sodium citrate (pH ~7) is added to the solution. The coacervated flavor is stirred for an additional 1.5 hours. The suspension of the coacervated butter flavor is stirred continually and fed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 386°F and outlet temperature of 194°F. The double encapsulated product was obtained as a free-flowing powder which has a yellow hue. DSC analysis shows the powder to be in a glassy state with a Tg of ~ 58°C.

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Example 4.

A coacervate was prepared as follows: A 1.0 liter solution of 6.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel F50) is prepared and held at 23°C. Then 72.6 grams of a lemon oil (Citrus and Allied, single fold) is slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer. After the emulsion has been prepared, 600 grams of solid maltodextrin (Lodex-10, American Maize Co.) is added slowly with continuous stirring. The coacervated flavor is held for an additional 1.5 hours. The lemon oil coacervate suspension is stirred and feed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 374°F and outlet temperature of 209°F. The double encapsulated product was obtained as a free-flowing amorphous powder.

Example 5.

A complex coacervate was prepared as follows: Gelatin (Type A, 275 Bloom) 45.0 grams was dissolved in 440 ml of distilled water held at 50°C. Sodium carboxymethylcellulose (4.5 grams) was dissolved in 220 grams of distilled water at 50°C. The two solutions were combined and the solution cooled to 35°C. Then 360 grams of liquid vegetable oil containing 0.1% D&C Violet #5 Dye was employed as the core material. The colored oil was emulsified employing an Arde Barinco homogenizer set at 40% of full power for approximately two minutes. After the oil was

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completely dispersed, an additional 2 liters of distilled water at 35°C was added, and the solution was cooled to ambient temperature and held for 2 hours. The solution was cooled to 10°C, and 5.6 grams of a 50 wt.% glutaraldehyde solution was added to cross-link the capsule wall. The sample was split into to equal batches and allowed to stir overnight.

One sample (1600 ml) was retained as a control. The second sample was brought to 40% added solids content by the slow addition of 246 grams of a 1:1 (wt.:wt.) mixture of 15 DE maltodextrin-sodium hexametaphosphate. Both samples were then spray dried in a pilot plant spray drier under identical pumping feed rates, nozzle rpm, inlet and collection air temperatures. The control sample was obtained as very porous powder in approximately 21% yield based on the original solids content and had a solid density of 0.98 g/cc. The double encapsulation sample was obtained as a free flowing powder in 31% yield (based upon coacervate) and 83% yield based upon total system solids. This material had a solid density of 1.32 g/cc. Evaluation of the encapsulated material by microscopy shows uniform spherical particles with interior coacervate cores as both single and multiple droplets within the macroparticle.

A series of dissolved solids were tested by spray drying the coacervate system as reported in Example 5. The response of the materials to the process and the resultant character of the double encapsulated solid products are given in Table 1:

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TABLE 1

RESPONSE OF COACERVATE-ADDED SOLIDS SUSPENSION TO SPRAY DRYING

Carrier #	Solutes Solids Added (40%)	Particle Density* (g/cc)	Spray Dried Product Character
1	(0%) Control	0.98	porous powder, limited recovery from dryer
2	(1:1) 15 DE Maltodextrin sodium hexametaphosphate	1.32	free flowing powder, spherical particles with uniform walls around core
3	15 DE Maltodextrin	0.83	free flowing powder, spherical macroparticle with uniform wall around core
4	24 DE Corn Syrup Solids	1.14	free flowing powder, larger individual particles
5	Maltose	1.22	Amorphous solid, large agglomerated particles, poor recovery in dryer
6	Sucrose/Glucose/Maltose (1:1:1)	1.29	adhesive solid, large agglomerated clumps of multiple particles
7	Citric Acid-Sodium Citrate (4:1)	1.58	Glassy solid (Tg=40°C) Significant coating on drier wall, agglomerated particles.

*Particle Density measurement reported as average of 5 trials per sample using Micromeritics AccPyc 1330 pycnometer

Example 6.

A complex coacervate was prepared as follows: 26.4 gm of Gelatin (Type A, 275 Bloom) was dissolved in 213.6 ml of deionized water by heating and holding the solution at 50°C. Then 26.4 gm of gum arabic was dissolved in 213.6 gm of deionized water also heated to 50°C. A core material consisting of 160 grams of a vegetable oil containing 0.05 wt.% FD&C Violet 2

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dye was added with stirring to the gum arabic solution at 48°C. The gelatin solution was then combined with the emulsified oil - gum arabic solution with the temperature maintained at 48°C. Following several minutes of stirring, 1500 ml of deionized water heated to 49°C was added over a period of 5 minutes to the gum arabic-gelatin emulsion system. The pH is adjusted to pH ≈ 4.20 with dilute acetic acid. The system is stirred continuously and allowed to quiescent cool to ambient temperature over a 2 hour period. The system is then cooled to 10°C by placing the batch container in a cooling bath. The pH is adjusted to 6.8 by addition of a dilute sodium citrate solution, and 5 ml of a 50 wt.% glutaraldehyde solution added, and the system held at 10-11°C for an additional hour and allowed to warm to ambient temperature overnight. A 1200 ml aliquot of the coacervation solution was taken, and 400 grams of a 60:40 mixture 10 DE maltodextrin- maltose monohydrate was slowly added with mixing. The coacervate-carbohydrate solution was dried in a pilot plant spray drier with inlet temperature set at 381°F and an outlet temperature of 232°F. A fine powder exhibiting a uniform violet color was obtained. Microscopic examination shows the color intensity concentrated in the coacervated oil droplet with no indications of free oil droplets.

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Example 7.

A complex coacervate was prepared according to the following procedure: 440 ml of a 1.4 wt.% gum arabic solution was prepared and used to emulsify 300 grams of an orange oil (Citrus and Allied, single fold) by homogenization with an Arde Barinco laboratory homogenizer. Then 440 ml of a 1.4 wt.% gelatin (Type A,200 Bloom) solution at 36°C was added to the emulsified orange oil-gum arabic system also held at 36°C.

The solution was adjusted to pH 4.0 by dropwise addition of a 30 wt.% acetic acid solution and the coacervate allowed to form by holding the system at ambient temperature for 1 hour. Then 6.0 grams of a 50 wt.% aqueous glutaraldehyde solution was added to crosslink the coacervated shell phase. After standing under gentle stirring for 15 hours, the sample was divided into two lots. To one lot of approximately 1600 ml was slowly added with stirring 1052 grams of a 1:1 mixture of sodium hexametaphosphate-15 DE maltodextrin solids over a period of one-half hour. The two lots, control and solids added dispersion were spray dried in a pilot plant unit under identical process parameters. The recovered dried products were obtained as fine powders. The yield of recovered control sample was 11% on a total solids basis, while the double encapsulated sample yield was 58% on a total solids basis.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.

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It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise as specifically described herein.

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CLAIMS:

1. A process for preparing a flavorant composition, comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in liquid;

(ii) adding an edible solute to said first suspension, to obtain a second suspension, in an amount such that the content of said edible solute in said second suspension is 5 to 55 wt.% based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying to obtain said flavorant composition.

2. The process of Claim 1, wherein said flavoring agent is selected from the group consisting of the lemon oil, orange oil, tangerine oil, anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil, spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; onion oil, leek oil, chive oil, garlic oil, butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols,

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ketones, esters, aldehydes and fatty acids, and extracts of reaction flavors, fruits and vegetables.

3. The process of Claim 1. wherein said microencapsulation is carried out by simple coacervation.

4. The process of Claim 1, wherein said microencapsulation is carried out by simple coacervation utilizing methylcellulose or hydroxypropylmethylcellulose as a water-soluble polymer and a carbohydrate oligomer having a D.E. in the range of 2 to 42 as a cosolute phase-separation inducing agent in an aqueous media.

5. The process of Claim 1, wherein said microencapsulation is carried out by complex coacervation.

6. The process of Claim 1, wherein said flavoring agent is a flavor oil.

7. The process of Claim 1, wherein said edible solute is added in an amount such that the content of said edible solute in said second suspension is 20 to 45 wt.% based on the total weight of said second suspension.

8. The process of Claim 1, wherein said coacervation is carried out with (i) methylcellulose or hydroxypropylmethyl cellulose; and (ii) a maltodextrin (5 to 15 D.E.), corn syrup solids (20 to 42 DE), sodium polyphosphate, or mixtures thereof.

9. The process of Claim 1, wherein said edible solute is selected from the group consisting of mono- and disaccharides, corn syrup solids, maltodextrans, modified starches, hydrolyzed gelatin, polydextrose, polyols, citric acid, sodium citrate,

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sodium and potassium chloride, sodium polyphosphates, and mixtures thereof.

10. A flavorant composition prepared by a process, comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid;

(ii) adding an edible solute to said first suspension, to obtain a second suspension, in an amount such that the content of edible solute in said second suspension is 5 to 55 wt.% based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying to obtain said flavorant composition.

11. The composition of Claim 9, wherein said flavoring agent is selected from the group consisting of the lemon oil, orange oil, tangerine oil, anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil, spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; onion oil, leek oil, chive oil, garlic oil, butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols, ketones, esters, aldehydes and fatty acids, and extracts of reaction flavors, fruits and vegetables.

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12. The composition of Claim 10, wherein said microencapsulation is carried out by simple coacervation.

13. The composition of Claim 10, wherein said microencapsulation is carried out by simple coacervation utilizing methylcellulose or hydroxypropylmethylcellulose as a water-soluble polymer and a carbohydrate oligomer having a D.E. in the range of 2 to 42 as a cosolute phase-change inducing agent in an aqueous media.

14. The composition of Claim 10, wherein said microencapsulation is carried out by complex coacervation.

15. The composition of Claim 10, wherein said flavoring agent is a flavor oil.

16. The composition of Claim 10, wherein said edible solute is added in an amount such that the content of said edible solute in said second suspension is 20 to 45 wt.% based on the total weight of said second suspension.

17. The composition of Claim 10, wherein said edible solute is selected from the group consisting of mono- and disaccharides, corn syrup solids, maltodextrins, modified starches, hydrolyzed gelatin, polydextrose, polyols, citric acid, sodium citrate, sodium and potassium chloride, sodium polyphosphates, and mixtures thereof.

18. The composition of Claim 10, wherein said composition is in the glassy state.

19. A method for encapsulating a flavorant, comprising:

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(i) mixing said flavorant in an aqueous medium with a polymer selected from the group consisting of methylcellulose and hydroxypropylmethylcellulose to obtain a mixture; and

(ii) adding a phase-separation inducing agent selected from the group consisting of maltodextrins, corn syrup solids, and mixtures thereof to said mixture to effect coacervation.

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Figure 1

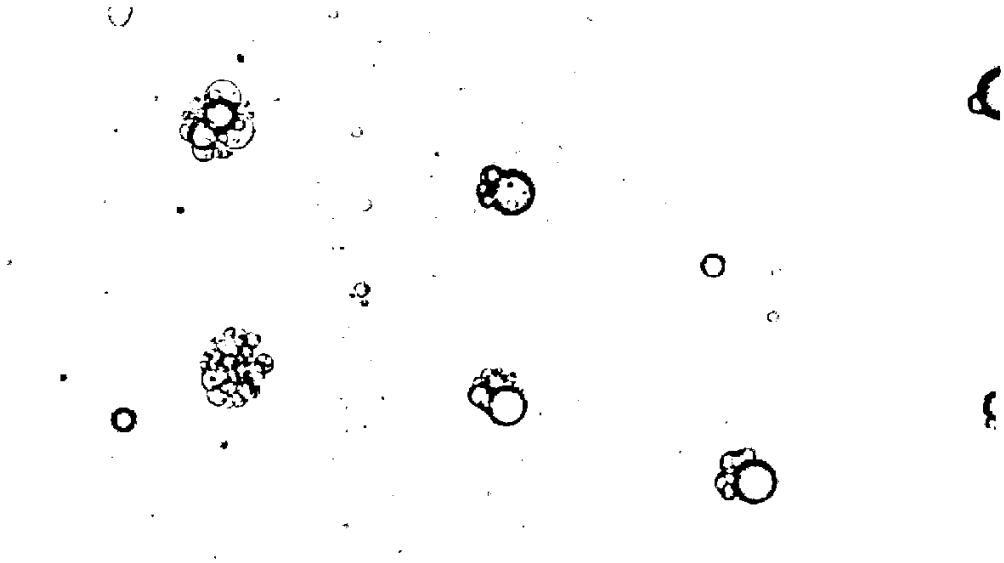
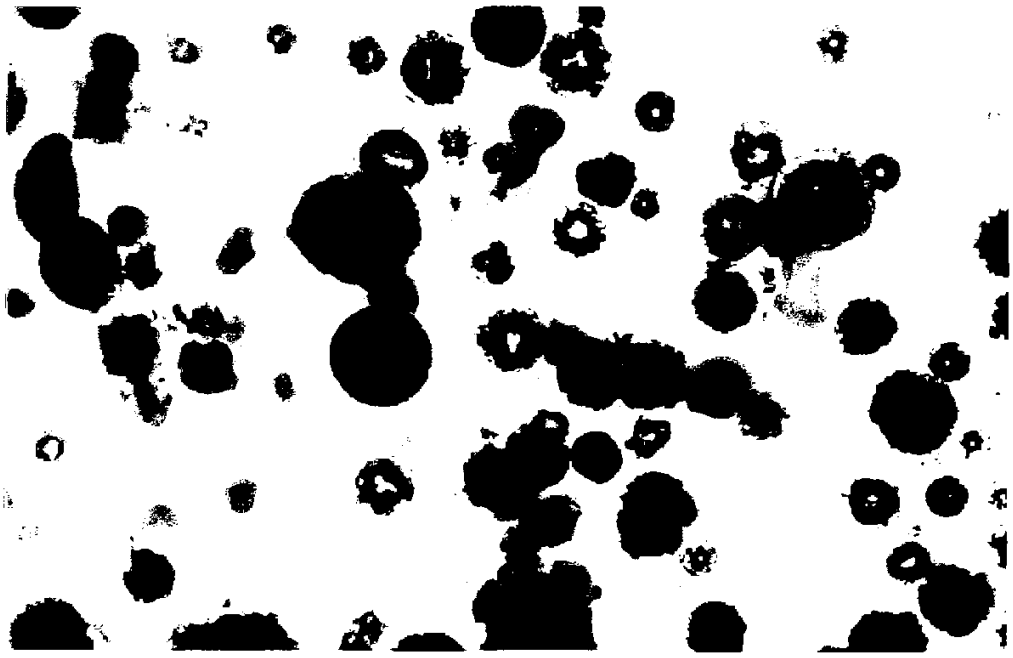


Figure 2



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A23L 1/221
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/103, 89, 96, 98, 650, 551

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, 93/19622 (PEARL ET AL.) 14 October 1993 (14.10.93), page 5 lines 15-26, page 8 lines 1-20 and page 9 lines 3-5.	1-19
Y	US, A, 5,087,461 (LEVINE ET AL) 11 February 1992 (11.02.92), see col. 6 lines 1-68.	1-19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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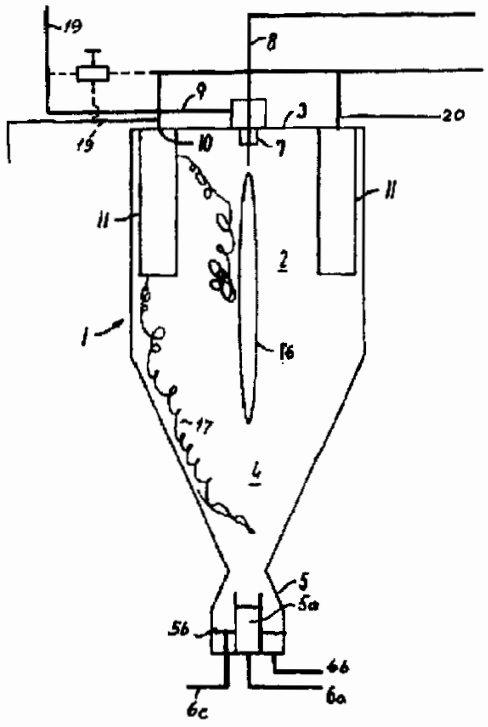
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(54) Title: SPRAY DRYING METHOD AND APPARATUS AND CLEANING METHOD FOR SUCH AN APPARATUS

(57) Abstract

In fluidized spray drying of a feedstock to produce an agglomerate product by means of at least one spraying device (7) arranged in the upper part (2) of a vertically disposed drying chamber (1), in a lower part of which a fluid-bed is accommodated, a drying gas introduced into a processing zone (16) of the chamber (1) is exhausted through an integrated arrangement of filter elements (11) in the upper chamber part (2) to retain and allow agglomerationof the particles carried by the flow of drying gas on the filter elements (11). By intermittent supply of reverse flow gas pulses to the filter elements (11) the retained particles are released and returned to agglomeration zones (16, 17). The drying gas is introduced at a rate producing at the filter walls (13) a flow rate amounting to at least 150 cubic meters per hour per square meter of filter wall surface. In the non-operative condition of the spray drying apparatus the filter elements (11) may be cleaned-in-place by supplying a cleaning liquid to the interior of the elements.



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Spray drying method and apparatus and cleaning method for such an apparatus.

This invention relates to a method of spray drying a feedstock to produce an agglomerated product, comprising the steps of supplying said feedstock to at least one spraying device arranged in the upper part of a vertically disposed drying chamber, introducing a drying gas into a processing zone of the chamber outside said spraying device, forming a layer of fluidized particles in a lower region of the chamber and exhausting said drying gas from the chamber through outlet means disposed in said upper chamber part.

Whereas the term "spray drying" refers, in general, to processes in which a fluid feedstock is at a relatively low temperature compared to the temperature of the drying gas, the feedstock may also be at a relatively high temperature with respect to the gas in processes which are sometimes referred to as "spray cooling". In the context of the present invention the generic term "spray drying" is used to encompass all such processes in which a fluid feedstock is sprayed into a drying gas.

Spray drying methods involving, in addition to the spraying of a liquid feedstock as small droplets of preferably uniform size distribution into a hot stream of drying gas, the use of a fluid bed integrated in the lower part of the drying chamber to expose the primary spray particles to further drying and classification are well known in the art and serves to produce a free flowing agglomerated product having desirable properties for many types of spray dried products such as dairy, food, pharmaceutical and chemical products, in particular socalled "instant" properties requiring high wettability and solubility and/or with specified

properties with respect to flowability and absence of small particles or fines, the presence of which in the product may cause handling problems and less acceptable conditions of occupational health in the performance of such methods.

Typically, these methods also known as the MSD™ or FSD™ process (Trademarks of NIRO A/S) involves the steps of atomizing a liquid feedstock into a spray of small droplets in the processing zone, where the droplets are contacted with the hot drying gas stream having a high velocity to produce partly dried primary particles, and formation of agglomerates by mixing the primary particles with fine or dustlike particles also known as fines, which are entrained from the drying chamber itself or returned to the agglomeration zones in the chamber from auxiliary equipment such as a cyclone outside the drying chamber, in which fines are retrieved from the exhaust of drying gas from the drying chamber, and subsequent additional drying in the fluid bed also serving to provide cooling of the agglomerated particles.

The main agglomeration zones in the chamber are the spraying zone or nozzle cloud immediately outside the spraying device, which is typically a spraying nozzle, the fluid bed which is typically located in the lower part of the chamber and on the inner surface of a conical part of the chamber, if present.

Typical prior art spray drying devices for the performance of the MSD and FSD methods as described can be found in published International Patent Application WO 95/24599, EP-B-097 484, EP-A-0 749 769 and EP-A-0 749 770 all of which suggest after-treatment of the product obtained from the fluid bed in a further fluid bed either by designing the fluid bed integrated in the drying chamber as a two stage fluid bed or arranging a

separate after-treatment fluid bed outside the drying chamber.

In many agglomeration processes the return of fines to the agglomeration zones of the drying chamber plays a significant role for the result to be obtained, and the properties of the agglomerated product will depend on many factors such as the part of the chamber to which fines are returned, such as discussed in EP-A-0 378 498 and WO 95/13864.

As disclosed therein as well as in EP-A-0 749769 conventional prior art suggestions for return of fines for use in an agglomeration process have suffered in general, however, from the disadvantage that the fines to be returned must be collected outside the chamber and transported to the chamber by a sometimes quite complicated ducting system.

Moreover, for a number of products incorporating poisonous, polluting or otherwise dangerous or hazardous chemicals such as a number of pharmaceutical products, dyestuffs etc. it is highly desirable and likely to become an environmental demand to improve safety by avoiding the handling of such materials outside the processing chamber.

In US-A-4,657,767, DE-A1-195 08 657 and DE-A1-195 11 961 the incorporation of integrated filter elements in dryers is disclosed per se. US-A-4,657,76 discloses a substantially horizontally disposed processing chamber with the spraying device and an arrangement of bag-type filter elements located at opposite ends of an upper chamber zone, whereby agglomerates formed to some extent on the filter elements are only dislodged to the region underlying the filter arrangement which is outside the main agglomeration zone. Also in DE-A-195 08 657 a horizontally disposed chamber is disclosed in which a filter wall extends throughout the chamber

above the processing zone without any precautions to dislodge material retained by the filter. DE-A1-195 11 961 discloses incorporation of filter elements in a direct flow drying chamber, substantially midway between a feeding device arranged in an upper part of the vertically disposed chamber and a fluid bed in the lower part thereof.

On this background, it is the object of the invention to provide a spray drying method involving the use of an integrated fluid bed and useful for production of agglomerated products of conventional or improved quality, which does not suffer from the above-mentioned disadvantages and provides important additional advantages with respect to a less complicated and more compact overall structure of the spray drying apparatus and in terms of facilitating cleaning of the apparatus, which is of significant importance when a spray drying apparatus is used for processing a range of different products requiring frequent cleaning and readjustment of the chamber.

According to the invention, this is obtained by a method of the kind defined which is characterized in that particles carried by the flow of drying gas towards said outlet means are retained by and allowed to agglomerate on a number of filter elements having substantially non-flexible filter walls and being arranged in the upper chamber part separated from said spraying device or devices and in flow communication with said outlet means, that reverse flow gas pulses are intermittently supplied to said filter elements to release retained particles therefrom to allow said particles to be returned to agglomeration zones in the chamber to participate in the agglomeration in said zones and that said drying gas is introduced at a rate producing at said filter walls a flow rate amounting to

at least 150 cubic meters per hour per square meter of filter wall surface.

By retaining the particles carried by the drying gas within the drying chamber itself the need for the complicated fines return systems involving the use of external cyclones or filters with associated pneumatic powder discharge and return transportation systems is completely eliminated.

The exhaust drying gas leaving the chamber is free from all particles, since they are retained by the filters and returned directly to take part in the agglomeration process in the chamber by the intermittent supply of the reverse flow gas pulses. Thereby, the method of the invention is very well suited for application to a socalled "closed cycle" process in which the exhaust drying gas is completely recirculated to the chamber after condensation and there are no gas discharges from the chamber, which is particularly useful for processes including the use of organic solvents or similar hazardous chemicals.

Contrary to the teaching of the prior art of the above-mentioned EP-A-0 378 498 as to the importance of selecting the right point in the drying chamber for the fines return, the invention has surprisingly shown a very good agglomeration of fine particles having suitable properties with respect to humidity, particle size etc. on the surfaces of filters integrated in the upper part of the drying chamber, said agglomeration acting in combination with the agglomeration in other zones of the chamber. In fact, the invention could rightfully be considered to add a new agglomeration principle which is useful in combination with the agglomeration principles known in the art. The agglomeration on the filter elements is moreover controllable by selection of the physical parameters with respect to

the filter loading by the drying gas and the supply of the reverse flow drying gas pulses.

It has further been demonstrated to be perfectly possible to design the integrated filters, which are preferably made with fairly rigid filtering walls of metallic, ceramic or polymeric materials or composites thereof, so that they will work well in the humid conditions prevailing in agglomeration dryers. The term "fairly rigid" is to be understood in the sense that the filtering walls could have a certain modest flexibility to provide for a better distribution of pressure forces.

Moreover, against a prevailing prejudice against exposing filters integrated in conventional drying chambers to a drying gas heavily loaded with particles, which are relatively moist and sticky, the invention has demonstrated that by appropriate arrangement and design of the filter elements and selection of process parameters such as the flow rate of the drying gas and the intermittent reverse gas cleaning pulses, blocking of the filters can be avoided to an extent making the method practical for continuous, contrary to batch-wise, FSD dryer operation.

The invention also relates to a spray drying apparatus for carrying out the method as defined above, comprising a vertically disposed drying chamber of substantially circular cross-section, in an upper part of which at least one spraying device is arranged together with feed means for supplying a feedstock and means for introducing a flow of drying gas into a processing zone of said chamber outside said spraying device or devices, whereas in a lower part of the chamber an integrated fluid bed is accommodated for forming and maintaining a fluidized layer of particles resulting from the spray drying performed by the apparatus,

outlet means for said drying gas being provided in said upper chamber part.

According to the invention, this apparatus is characterized in that a number of filter elements having substantially non-flexible filter walls are arranged in said upper chamber part separated from said spraying device or devices and in flow communication with said outlet means for retaining particles carried by said drying gas towards said outlet means, said filter elements communicating with a pressurized gas supply for intermittently supplying reverse flow pulses of cleaning gas to the filter elements to release particles retained by the filter elements during operation of the spray drying apparatus, and that means are provided for introducing said flow of drying gas at a rate producing at the filter walls a flow rate amounting to at least 150 cubic meters per hour per square meter of filter wall surface.

Advantageous embodiments of such an apparatus will appear from dependant claims 7 to 16.

A significant advantage of the method and apparatus of the invention comes from the facilitated possibilities for cleaning-in-place of the integrated filters in the non-operative condition of the apparatus allowing for a reduction of the period of non-operation needed for such a cleaning.

Therefore, the invention further relates to a method of cleaning the apparatus which is characterized in that a cleaning-in-place of the filter elements is performed in a non-operative condition of the spray drying apparatus by supplying a cleaning fluid in reverse flow through the filter elements.

Preferably, this cleaning-in-place of the filter elements and cleaning of the interior of the drying chamber are performed in a single coherent process.

In the following the invention will be described in further detail with reference to the accompanying drawings, in which

figure 1 is a schematical section of a spray drying apparatus embodying the invention;

figure 2 shows an embodiment of an arrangement of filter elements for use in the apparatus in figure 1;

figure 3 shows an embodiment of an individual filter element;

figure 4 a cross-sectional view of a modification of the filter element in figure 3;

figure 5 shows an alternative arrangement of filter elements.

In figure 1 a vertically disposed drying chamber 1 for a spray drying apparatus is shown which comprises a mainly cylindrical upper chamber section 2 with a ceiling 3 and a lower conical chamber section 4 at the bottom of which a fluid bed arrangement 5 of a design known per se is located with supply lines 6a and b for supplying drying and/or cooling gas to a back-mix section 5a and a plug-flow section 5b of the fluid bed arrangement 5, respectively, and a product discharge line 6c.

The fluid-bed arrangement may thus be of the two-stage type disclosed in WO 95/24599, and as disclosed in EP-A-0 749 770 the drying chamber need not be designed with a lower conical section for accommodation of the fluid-bed, but could have an overall cylindrical form. The fluid bed arrangement may also be a single stage fluid bed.

In the illustrated embodiment a single nozzle-type spraying device 7 is arranged in the upper part of the cylindrical upper section immediately below the chamber ceiling 3 to which a supply line 8 for the fluid feedstock to be processed in the chamber is connected.

The spraying device 7 could also be suspended, however, a certain distance below the ceiling 3. The fluid feedstock may typically be a liquid dispersion or suspension, but could also be a powder product supplied as feed for a rewetting process by being exposed to wetting by a typically aqueous liquid supplied to a spraying distributor, such supplying and spraying means constituting the spraying device. Rewetting processes are typically used in practice e.g. for coffee powder agglomeration by steam and water, using e.g. a three fluid nozzle as mentioned in the foregoing, or rewetting/mixing a supplementing powder with an agglomerating feedstock containing the main part of the total solids content of the end product.

For liquid feedstocks the spraying device 7 may be of the high pressure nozzle-type or of the two-fluid or three-fluid (e.g. gas, steam, feedstock) types. The spraying device may also be a rotating distributor, e.g. a wheel or cup in such designs as known in the art.

Together with the spraying device 7 supply means 9 for introduction of a drying gas, which in the example illustrated may be a hot drying gas typically having a temperature between 100° and 550°, is connected with the central part of the chamber ceiling 3. The velocity of the drying gas may be varied within wide limits depending on the actual selection of spraying device.

Connected to a peripheral region of the chamber ceiling 3 is an outlet system for the drying gas comprising an exhaust manifold duct 10.

In the illustrated embodiment a number of discrete filter elements 11 are connected to the chamber ceiling 3 and may be arranged, symmetrically around the spraying device 7, as shown in figure 2, and in flow com-

munication with the exhaust manifold duct 10. The filter elements need not necessarily be connected to the ceiling 3, but could also be secured in the upper part of the cylindrical chamber wall.

Moreover, the individual filter elements need not be identical in shape and size, but could be of different designs and sizes.

The invention may also be applied, however, to spray drying chambers in which several spraying devices are used, and in such cases the spraying devices could be arranged centrally in the way described, but could also be arranged symmetrically around a central arrangement of filter elements or a single filter element.

As shown in more detail in figure 3 the individual filter elements 11 may be of an elongate, preferable substantially cylindrical form closed at the bottom and connected at the top with a fixture 12 to be secured to the chamber ceiling 3. Each filter element has an active filtering wall 13 which is preferably made of a fairly rigid metallic, ceramic or polymeric material, preferably a sintered metallic material like sintered stainless steel fibres as disclosed in the Article "Sintered Metal Filter Elements for Use with Dryers and Mills in the Pharmaceutical Industry" , Filtration & Separation, Nov/Dec 1996 pages 881-891.

The arrangement of the filter elements can be operated at a high specific loading with respect to the flow rate of the drying gas exhausted through the filter elements. According to the invention the drying gas is introduced into the chamber at a rate producing at the filter walls 13 a flow rate amounting to at least 150 cubic meters per hour per square meter of the surface of the filter walls 13. Flow rates of this magnitude are substantially beyond the drying gas loading conventionally used for bag filters, but has

turned out to be an essential feature of the invention to obtain a high specific powder loading of the filter walls, which is important for the agglomeration process. The flow rate should preferably be more than 180 and most preferably in the range of 200 - 600 cubic meters per hour per square meter of the surface of the filter walls 13.

In order to provide an intermittent supply of reverse flow cleaning gas pulses to the interior of each filter element 11 during operation of the spray drying apparatus, the interior of the filter elements 11 is in flow communication with a pressurized air supply, which in figure 3 is illustrated by the arrangement of a pressurized air nozzle 14 immediately outside the exhaust gas outlet 15 of each filter element. In a manner known per se, the outlet 15 may provide a venturi-shaped inlet for the intermittently supplied reverse flow pulses.

The filter elements 11 may be designed in other shapes than shown. In order to increase the active surface of a filter element 11a it could as a modification to a cylindrical wall be advantageous, for example, to give the filter wall 13a a surface increasing profiled shape such as the pleated surface shown in the cross-sectional view in figure 4.

As further illustrated in the cross-sectional view in figure 5 the filter elements 11b may form separate sections of a single coherent filter assembly 21 having a cylindrical inner and outer wall surface 22 and 23 facing the spraying device 7a and forming the filter wall 13b. The filter could also be annular and be placed in roof or the chamber wall.

In the illustrated spray drying apparatus a fluid feedstock supplied to the nozzle-type spraying device 7 will be atomized to droplets which in the underlying

nozzle cloud zone 16 of the chamber will be exposed to drying by the drying gas supplied from supply line 9. In the same zone an agglomeration of particles starts and in result heavier particles and agglomerates fall by gravity or by being carried by the drying gas flow towards a further agglomeration zone 17 at the wall of the conical chamber part 4 and towards the fluid-bed 5, whereas fines are carried by the upwards flow of drying gas towards the integrated filter elements 11 to be retained on the surfaces thereof, where also an agglomeration of these particles will take place.

The particles and agglomerates formed on the outer surfaces of the filter elements 11 are as already described released intermittently by supplying reverse flow pulses of pressurized air or gas to the interior of the filter elements 11 through the nozzle means 14 in figure 3. The released particles and agglomerates will fall down into the agglomeration zones formed by the nozzle cloud 16 or dependant on their weight further on to the zone 17 at the wall of the conical chamber part 4 or to the fluid-bed 5.

The supply of the reverse flow cleaning pulses of pressurized air or gas is controlled by means of valves 18 in the pressurized air supply line 19 leading to the nozzles 14 in figure 3 and is typically generated as short bursts of a duration of 0,05-5 sec. with intervals between 1 sec. and 30 minutes and at a pulse pressure of 1 - 10 bar.

As a special feature of the invention the integrated filter arrangements of elements 11 provides an attractive and advantageous possibility for cleaning-in-place of the filter elements 11 between periods of operation by supplying a cleaning or washing liquid to the interior of each filter element 11 through a supply line 20. This cleaning procedure are supported by

supplying reverse flow pulses to promote distribution of the cleaning liquid over the entire internal surface of the filter walls 13 by mixing the cleaning liquid with the gas flow pulses in the nozzle means 14 outside the venturi inlet 15 of each filter element 11, as shown in figure 3 immediately before spraying.

As an important advantage the cleaning of the filter elements 11 may be performed concurrently with cleaning of the interior of the processing chamber by means not illustrated in the drawings in a single coherent process. Whereby the cleaning of the filter elements 11 from the inside may be assisted by a simultaneous washing of the external side of the filter elements 11.

As shown in dashed lines in figure 1 the supply of air or gas to nozzles 14 in figure 3 for generation of the reverse flow cleaning pulses may advantageously be taken from the inlet supply 8 of drying gas or from the drying gas outlet, i.e. from the exhaust manifold 10 or in any combination thereof, whereby a separate pressurized air or gas supply can be dispensed with.

The efficiency of method and apparatus of the invention will be illustrated by the following examples

Example 1:

Fluidized spray drying of Maltodextrine was performed under the following drying conditions:

Drying gas inlet temperature:	150-180°C
Drying gas outlet temperature:	60-70°C
Inlet temperature to fluid-bed back-mix section:	90°C
Inlet temperature to fluid-bed plug-flow section	60°C
Nozzle pressure:	1.3-1.8 bar

Nozzle air/feed ratio:	0,6-0,7
Drying gas flow rate at filter wall	166-255 m/hour
Feed characteristics:	30 % DM solution at 20°C

The following product characteristics were obtained:

Bulk density: (untapped)	0.35-0.45 kg/l
Bulk density (tapped 100x)	0.40-0.52 kg/l
D_{50} (<50%)	250 - 300 µm
D_{10} (<10%)	130 - 160 µm
Fines (< 90 µm)	0.5 - 0.9 %
Moisture	3 - 5 %

Primary particles were obtained with a particle size ranging from 20 to 80 µm verifying agglomerates consisting of a great number of primary particles and a high collision rate between wet particles and partly dried fines.

Example 2:

Fluidized spray drying of a dairy product was performed under the following drying conditions

Drying gas inlet temperature:	150-190°C
Drying gas outlet temperature:	65-75°C
Inlet temperature to fluid-bed back-mix section:	75°C
Inlet temperature to fluid-bed plug-flow section	45°C
Nozzle pressure:	1.3-1.8 bar
Nozzle air/fluid ratio:	0,5-0,9
Drying gas flow rate: at filter wall:	166-255 m/hour
Feed characteristics:	41 % DM solution at 50°C

The following product characteristics were obtained:

Bulk density (untapped):	0.35-0.55 kg/l
Bulk density (tapped 100x):	0.40-0.65 kg/l
D_{50} (<50%):	220 - 260 µm
D_{10} (<10%):	110 - 150 µm
Fines (< 90 µm)	2 - 3 %
Moisture:	3 - 5 %

The primary particles produced were in the range from 20 to 60 µm.

PATENT CLAIMS

1. A method of spray drying a feedstock to produce an agglomerated product, comprising the steps of supplying said feedstock to at least one spraying device (7) arranged in the upper part (2) of a vertically disposed drying chamber (1), introducing a drying gas into a processing zone (16) of the chamber outside said spraying device, forming a layer of fluidized particles in a lower region of the chamber and exhausting said drying gas from the chamber through outlet means disposed in said upper chamber part, **characterized in** that particles carried by the flow of drying gas towards said outlet means are retained by and allowed to agglomerate on a number of filter elements (11) having substantially non-flexible filter walls (13) and being arranged in the upper chamber part (2) separated from said spraying device (7) or devices and in flow communication with said outlet means, that reverse flow gas pulses are intermittently supplied to said filter elements to release retained particles therefrom to allow said particles to be returned to agglomeration zones (16,17) in the chamber (1) to participate in the agglomeration in said zones and that said drying gas is introduced at a rate producing at said filter walls (13) a flow rate amounting to at least 150 cubic meters per hour per square meter of filter wall surface.

2. A method as claimed in claim 1, **characterized in** that said flow rate amounts to at least 180 cubic meters per hour per square meter of filter wall surface.

3. A method as claimed in claim 2, **characterized in** that said flow rate amounts to from 200 to 600 cubic meters per hour per square meter of filter wall surface.

4. A method as claimed in claim 1, 2 or 3, **characterized in** that said reverse flow gas pulses are formed from said drying gas as supplied to and/or exhausted from said chamber (1).

5. A method as claimed in one of the preceding claims, **characterized in** that said reverse flow gas pulses are generated as short bursts of a duration of 0.05-5 sec. with intervals between 1 sec. and 30 minutes and at a pulse pressure of 1 - 10 bar.

6. A spray drying apparatus for carrying out the method as defined above, comprising a vertically disposed drying chamber (1) of substantially circular cross-section, in an upper part (2) of which at least one spraying device is arranged together with feed means (8) for supplying a feedstock and means (9) for introducing a flow of drying gas into a processing zone (16) of said chamber outside said spraying device or devices, whereas in a lower part (4) of the chamber an integrated fluid bed (5) is accommodated for forming and maintaining a fluidized layer of particles resulting from the spray drying performed by the apparatus, outlet means (10) for said drying gas being provided in said upper chamber part (2), **characterized** in that a number of filter elements (11) having substantially non-flexible filter walls (13) are arranged in said upper chamber part (2) separated from said spraying device (7) or devices and in flow communication with said outlet means (10) for retaining particles carried by said drying gas towards said outlet means, said filter elements (11) communicating with a pressurized gas supply (19) for intermittently supplying reverse flow pulses of cleaning gas to the filter elements (11) to release particles retained by the filter elements (11) during operation of the spray drying apparatus, and that means are provided for introducing said flow

of drying gas at a rate producing at the filter walls a flow rate amounting to at least 150 cubic meters per hour per square meter of filter wall surface.

7. A spray drying apparatus as claimed in claim 6, **characterized in** that said filter elements (11) are further connected to a supply (20) of cleaning liquid to allow cleaning-in-place of the filter elements in a non-operative condition of the spray drying apparatus.

8. A spray drying apparatus as claimed in claim 7, **characterized in** that a nozzle (14) is arranged outside an inlet of each filter element (11), said nozzle (14) being connected with said pressurized gas supply (19) and said cleaning liquid supply (20) to effect mixing of the cleaning liquid with pressurized gas immediately prior to supplying said mixture to the interior of the filter element (1).

9. A spray drying apparatus as claimed in claim 6, 7 or 8, **characterized in** that said filter elements (11) are arranged around a single spraying device (7) arranged centrally in said upper chamber part (2).

10. A spray drying apparatus as claimed in claim 7, **characterized in** that said outlet means (10) are provided at a ceiling (3) of said chamber (1) and that each of said filter elements (11) is of a generally elongated form with one end secured to said chamber ceiling (3).

11. A spray drying apparatus as claimed in claim 9, **characterized in** that said filter elements form sections (11b) of a single filter assembly (21) having substantially cylindrical inner and outer filter walls (22, 23) facing said spraying device, said sections being separated by partitions.

12. A spray drying apparatus as claimed in any of claims 6 to 9, **characterized in** that a number of spraying devices are arranged symmetrically around a central

filter element or arrangement of filter elements.

13. A spray drying apparatus as claimed in any of claims 6 to 12, **characterized in** that said filter walls (13) are of a substantially rigid metallic, ceramic or polymeric material or a composite thereof.

14. A spray drying apparatus as claimed in claim 13, **characterized in** that said material is a sintered metallic material.

15. A spray drying apparatus as claimed in claim 13 or 14, **characterized in** that said filter walls (13a) have a surface increasing configuration.

16. A spray drying apparatus as claimed in any of claims 6 to 15, **characterized in** that said gas supply (19) for the filter elements is connected to an inlet (9) and/or said outlet means (10) for drying gas to use said drying gas at said inlet or said outlet means or any combination thereof to generate said reverse flow cleaning gas pulses.

17. A method of cleaning a spray drying apparatus as claimed in any of claims 6 to 16, **characterized in** that cleaning-in-place of the filter elements is performed in a non-operative condition of the spray drying apparatus by supplying a cleaning fluid in reverse flow through the filter elements (11).

18. A method as claimed in claim 17, **characterized in** that said supply of cleaning liquid is supported by an intermittent supply of pressurized gas pulses for enhanced distribution of said liquid over the internal surface of said filter walls (13).

19. A method as claimed in claim 17, **characterized in** that said cleaning liquid is mixed with said pressurized gas pulses immediately prior to being supplied to each filter element (11).

20. A method as claimed in claim 17, 18 or 19, **characterized in** that said cleaning-in-place of the

filter elements (11) and cleaning of the interior of the drying chamber (1) are performed in a single coherent process, whereby the supply of cleaning liquid to the interior of the filter elements (11) is assisted by washing of the external side of the filter elements.

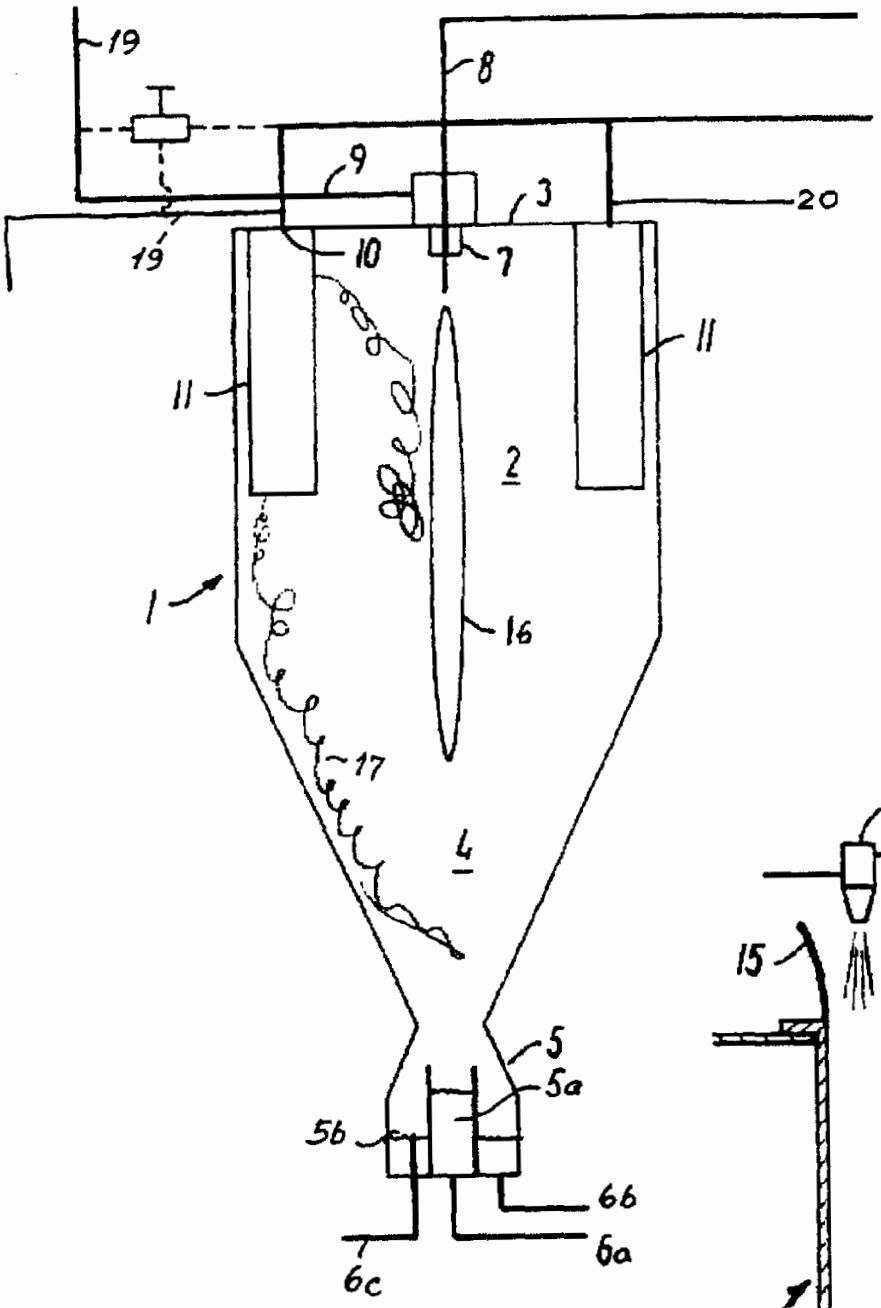


FIG.1

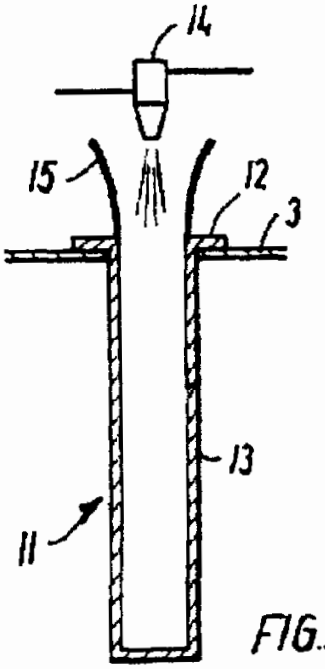


FIG.3

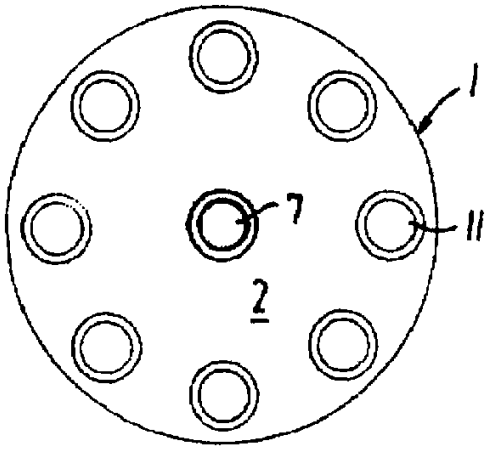


FIG. 2

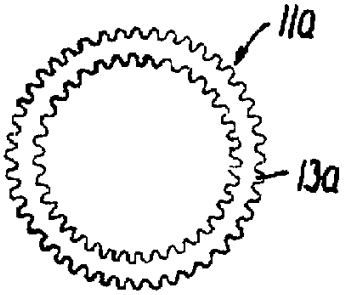


FIG. 4

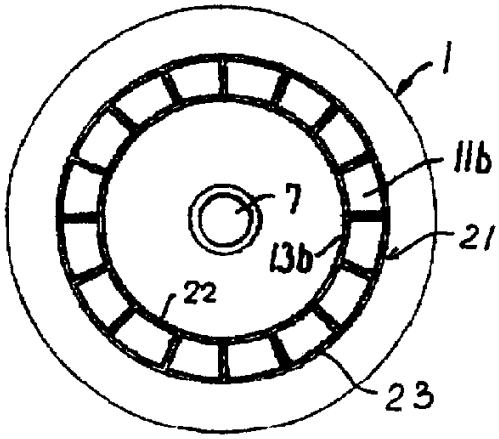


FIG. 5

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(54) Title: PREPARATION OF COLORED POWDERS/GRANULATES BY MEANS OF A FLUID BED DRYING APPARATUS

(57) Abstract

A method of making a colored food or pharmaceutical excipient using a fluid bed drying machine is disclosed. The colored excipients of the present invention have been found to have a uniform color appearance.

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PREPARATION OF COLORED POWDERS/GRANULATES BY MEANS OF A FLUID BED DRYING APPARATUS

BACKGROUND OF THE INVENTION

The present invention relates to powders/granulates, and more particularly colored powders/granulates, and the use of a fluid bed drying apparatus (with a spraying apparatus) for applying a suitable coloring agent to said powders/granulates.

Various fluid bed drying apparatus (with a spraying apparatus) are well-known in the pharmaceutical art [including, for example the Glatt (Model GPCG5) and the Aeromatic (Model S-7/1100L)] and are typically utilized to prepare granulates ("pellets") for use in preparing tablets or powders/granulates for oral suspension.

The spraying apparatus of fluid bed drying apparatus have been used to spray a binder liquid (e.g. starch paste) or coating liquid (e.g waxes, fats and oils) from a nozzle for granulating or coating while they are fluidized by a fluidizing gas introduced from the bottom of the apparatus of a fluid bed machine.

The basic design of a typical fluid bed drying machine is center around the product container. The product container is an inverted truncated cone which has a reinforced screen in its bottom. The purpose of the screen is to allow sufficient air flow through the product bed without product passing down through into the inlet plenum, or air handling section. Directly above the product container is a cylindrical deceleration zone called expansion chamber. As air bubbles pass through the product bed, particles are carried upwards into the expansion chamber where the air velocity quickly diminishes to the point where it can no longer entrain particles. The material travels toward the walls of the expansion chamber, drops back into the product container and continue its cycling. At some height in the expansion chamber a nozzle is placed for application of the spraying liquid. The liquid is sprayed at a controlled rate into the randomly fluidized powder.

The application of a colorant by means of the spray apparatus in a fluid bed drying machine has not been previously described.

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SUMMARY OF THE INVENTION

It has been surprisingly discovered that the use of the spray apparatus in a fluid bed drying machine provides a suitable means of preparing an elegant uniform fine powder having a color appearance of the sprayed excipient which is essentially the same in both solid and reconstituted form. The present invention provides a means of producing a colored excipient with a surprising color intensity and color uniformity with a small quantity of FDC approved color. The present invention includes methods of making colored excipients by means of spray drying of a colorant solution (can be a natural or synthetic FDC color, such as caramel, FDC Blue #1, Blue #2, Yellow #5, Yellow #6 and Red #40) to food and pharmaceutical excipients.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention can be utilized to spray a solution of a colorant (preferably a color approved for use with foods, drugs and/or cosmetics; for example caramel, beta carotene, FDC Blue #1, Blue #2, Yellow #5, Yellow #6 and Red #40), compatible with the excipient(s) to which it is to be applied.

The process variables of the present invention include:

1) Atomization air pressure
2) Liquid Spray rate
3) Product temp, inlet temperature
4) Nozzle pore size
5) Nozzle position
6) Batch size

and will vary depending upon the particular fluid bed machine utilized and the particle size of the particular excipient (powder/granulate) to be colored. The particle size of the excipient may vary from about 500 to 40 microns, preferably from about 500 to 40 microns. A person skilled in the art can readily determine the appropriate process variables so as to produce an elegant colored product.

The top spray apparatus of the fluid bed drying machine is positioned as low as possible above the bed of the machine in such a manner as to produce a uniform spray pattern.

The process parameters of the present invention, are typically:

Spray rate: production scale 200 Gm/min to 3000 Gm/min

Inlet temperature: 60 degree C to 100 degree C

Outlet temperature: 25 degree to 60 degree C

Atomization air: 1 bar to 7 bars, preferably greater than 3 bars

Batch temperature: above 45 degree C

The following Examples further illustrate the subject invention.

Example 1) Pink Electrolyte Powder

Formula:

Part A:

Dextrose USP Anhydrous	3.36 Kg
Sodium Citrate Hydrous USP	490 Gm
Sodium Chloride USP Powder, 150 mesh	195.3 Gm
Potassium Chloride USP Granule	252 Gm

Part B:

Aspartame NF Powder	28 Gm
FDC Red #40 Dye	0.35 Gm
Water	1000 Ml

Description of Process:

1) Weigh and screen through a #12 mesh screen all the ingredients.

2) dissolve the red #40 into the water, then suspend aspartame in the colored solution with agitation.

3) To the product container of a Glatt GPC5G fluid bed processor add all of ingredients of Part A.

3) Turn on the turbine, heat the batch until the bed temperature reaches 50 degree C. Start spraying the color/aspartame solution in accordance with the following parameters:

Spray rate: 32 Gm/min

Atomization air: 3 bar

nozzle pore: 1.8 mm

inlet air temp: 80 degree

product temp: 48-52 degree C

Outlet temp: 36-40 degree C

Nozzle position: lowest (about 10 inches above bed).

4) after spaying all of the liquid, dry the batch to 60 degree C in the fluid bed dryer.

If desired, a bubble gum flavor (e.g. Robertet NV16508; 150 mg/unit dose) can be added to the colored formulation prepared above.

The flavored/unflavored electrolyte formulation can be packaged in unit-of-use packets containing about 6180 mg (each containing about 279 mg. NaCl, 700 mg. Sodium Citrate, 360 mg. KCl, 4800 mg dextrose, 40 mg aspartame and 0.5 mg FDC Red #40). Each packet can be dissolved in about eight ounces of water and taken orally for electrolyte replacement.

Example 2) Pink Bubble Gum Dextrose

Formula:

Part A:		
Dextrose USP (Anhydrous)	492.8	Kg
Part B:		
FDC Red #40 dye	51	Gm
Purified Water	40	liter

Description of Process:

1) Dissolve dye into water.

2) To the Aeromatic S7 (**1100L**) product container add the Dextrose [preferably the dextrose having been delumped through a Comil model 196 with #2F083R037/42 screen; impeller number 2F 1601 175 or 2F 1601 221].

3) Turn on the turbine, heat the batch until the exhaust temperature reaches 50 degree C. Start spraying as the colorant according to following parameters:

spray rate: 800 Gm/min

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Atomization air: 5-6 bars
inlet air temp: 100 degree C
outlet air temp: 50 degree C - 60 degree C
Nozzle pore: 1.8 mm
nozzle head: triple head
Nozzle position: lowest possible

The position of spray arms is such that the nozzle head is at the same height or just below the rolled "V" groves (bottom of the exhaust filter.

Note: a dehumidification system is utilized and the dew point allowed to stabilize at about -5 to about -20 degrees C or below.

4) After spraying all of the solution, dry the product 65 degree C. in the fluid bed dryer.

If desired, a bubble gum flavor (e.g. Robertet NV16508) and/or aspartame can be added to the pink colored dextrose.

An electrolyte replacement product can be prepared utilizing the pink colored/flavored dextrose of this Example by adding milled salts to an Alma Blender:

Sodium Chloride USP Powder	52.9 Kg
Potassium Chloride	68.3 Kg
Sodium Citrate Hydrous USP	132.7 Kg
Aspartame NF Powder	7.6 Kg

and 910 KG. of colored/flavored dextrose.

The colored/flavored dextrose is delumped through a Comil Model 196 (with #2F045R031\37 screen and impeller number 2F 1601 175 or 2F 1601 221).

The salts are premilled by a Comil Model 196 (with #2F024R018\23 screen and impeller number 2F 1601 175 or 2F 1601 221) before blending into the batch for 30 minutes.

The electrolyte replacement product can be packaged in unit-of-use packets containing about 6180 mg (each containing about 279 mg. NaCl, 700 mg. Sodium

Citrate, 360 mg. KCl, 4800 mg dextrose, 40 mg aspartame and 0.5 mg FDC Red #40). Each packet can be dissolved in about eight ounces of water and taken orally for electrolyte replacement.

Example 3) Grape Colored Dextrose

Formula:

Part A:		
Dextrose USP Anhydrous	441.3	Kg
Part B:		
FDC Red #40	55	Gm
FDC Blue #1	18	Gm
Purified water	40	Kg

Description of Process:

1) Dissolve color in purified water.

2) To the product container of a Aeromatic S7 **(1100L)** add dextrose [preferably the dextrose is delumped through a Comil model 196 with #2F045R031/37 screen].

3) Turn the turbine on, heat the batch to 60 degree C and start spraying as following

spray rate : 800 gm/min
atomization air: 5-6 bars
inlet air: 100 degree C
outlet air: 50 - 60 degree C
nozzle pore; 1.8 mm
nozzle head: triple heads
nozzle position: lowest possible

4) After all of the liquid is sprayed, dry the batch to 65 degree C. in the fluid bed dryer.

If desired, a grape flavor (e.g. Florasynth WL-26112; 300 mg/unit dose) and/or aspartame can be added to the grape colored dextrose.

An electrolyte replacement product can be prepared utilizing the grape colored/flavored dextrose of this Example by adding milled salts to an Alma Blender:

Sodium Chloride USP Powder	51.3Kg
Potassium Chloride USP Granule	66.5 Kg
Sodium Citrate Hydrous USP	129 Kg
Aspartame NF Powder	14.7 Kg

and 883 KG. of colored/flavored dextrose.

The colored/flavored dextrose is delumped through a Comil Model 196 (with #2F045R031/37 screen and impeller number 2F 1601 175 or 2F 1601 221) and then added into the blender.

The salts are premilled by Comil Model 196 (with #2F024R018/23 screen and impeller number 2F 1601 175 or 2F 1601 221) before blending into the batch for 30 minutes.

The electrolyte replacement product can be packaged in unit-of-use packets containing about 6180 mg (each containing about 279 mg. NaCl, 700 mg. Sodium Citrate, 360 mg. KCl, 4800 mg dextrose, 40 mg aspartame and 0.5 mg FDC Red #40). Each packet can be dissolved in about eight ounces of water and taken orally for electrolyte replacement.

Claims:

1. A method of producing a colored excipient comprising the steps of:
a) preparing a color solution and
b) applying said color solution to an excipient by means of a spray head apparatus in a fluid bed drying machine.

2. The process of Claim 1 where the color solution is prepared from one or more FDC or natural colors selected from the group consisting of caramel, beta carotene, blue #1, blue #2, yellow #5, yellow #6, and Red #40.

3. The process of Claim 2 where the FDC color is Red #40.

4. The process of Claim 2 where the FDC color is Blue #1.

5. The process of Claim 2 where the FDC colors are Red #40 and Blue #1.

6. The process of Claim 1 where the FDC color is Red #40 and the excipient is a mixture of dextrose, sodium chloride, sodium citrate and potassium chloride.

7. The process of claim 1 where the color solution consists of one or more colors and the excipient is a food or pharmaceutical ingredient.

8. The process of claim 1 where the color solution consists of one or more colors and the excipient is dextrose.

9. An electrolyte replacement product containing a colored excipient, said colored excipient prepared by applying a color solution to an excipient by means of a spray head apparatus in a fluid bed drying machine.

10. An electrolyte replacement product in accordance with Claim 9 containing about 279 mg. NaCl, 700 mg. Sodium Citrate, 360 mg. KCl, and 4800 mg dextrose.

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11. An electrolyte replacement product in accordance with Claim 9 wherein dextrose is a colored excipient.

12. An electrolyte replacement product in accordance with Claim 9 wherein dextrose is colored with a color solution containing FDC Red #40.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K9/14 A61K9/16 A23L1/275

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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Int. ional Application No
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[Continued on next page]

(54) Title: PROCESS FOR PREPARING SHELF STABLE CUSTARD APPLE PULP AND POWDER

(57) **Abstract:** The present invention deals with an organic process for preparing pulp from custard apple, which has an extended storage life of 12 months in a frozen state in acceptable conditions that can find use in various applications during non-availability of the fruit and a custard apple powder free of bitterness, discoloration and off-flavor and that can be used in chilled beverages and ice creams. The process for preparing frozen custard apple pulp comprising mixing custard apple pulp with 0.05 to 0.15% ascorbic acid, filling in containers and blast freezing. The obtained pulp can also be mixed with milk powder, sugar candy, maltodextrin, tricalciumphosphate and honey, and spray dried.

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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*

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PROCESS FOR PREPARING SHELF STABLE CUSTARD APPLE PULP AND POWDER

TECHNICAL FIELD:

The present invention relates to a process for preparing shelf stable custard apple pulp and custard apple powder. The present invention deals with an organic process for preparing pulp from custard apple, which has an extended storage life of 12 months in a frozen state in acceptable conditions that can find use in various applications during non-availability of the fruit. The present invention also deals with an organic process for preparing custard apple powder free of bitterness, discoloration and off-flavor and that can be used in chilled beverages and ice creams.

BACKGROUND OF THE INVENTION:

The custard apple is a delicious tropical fruit. The white, creamy flesh has a strong aroma reminiscent of a mixture of strawberry, banana and pineapple. The fruits are generally eaten raw only when ripe, as heating alters the flavor. The fruits are highly perishable, and do not stay long after ripening. In view of seasonal availability and fast perishability of the fruit, a process for storage of good quality fruit pulp was attempted. During off-season, the stored pulp finds use in various applications like making ice cream, milk shakes, RTS beverages, nectar and so on.

In reference by Pardede *et al.,* (1994) Food - Australia 46(5) : 205 - 206 wherein, treated custard apple pulp with 0.1% ascorbic acid can be stored up to 3 months in sealed nylon/LDPE bags at - 16.3°C.

In another reference by Gamage *et al.,* (1997) Journal of Food Processing and Preservation 21(4) : 289 - 301 wherein, storage life of 1 month was recorded for custard apple pulp when the pulp was treated with 0.1 - 0.5% ascorbic acid and stored in polyethylene bags at 0°C.

There however does not exist any prior art that teaches a process for preparing custard apple powder and no such product is available in the market.

OBJECTS OF THE INVENTION:

The main object of the present invention is to provide a process for the preparation of shelf-stable custard apple pulp

Another object of the present invention is to achieve the storage life of custard apple pulp in frozen form for as long a period as 12 months.

Yet another object is to achieve the storage life of custard apply pulp in organic state without the use of any chemical, other than ascorbic acid.

Still another object is to maintain the pulp in a form free of discoloration, off-flavor and development of bitterness, while use in thawed form.

One more object of the present invention is to provide a process for preparing custard apple powder that is free of bitterness, discoloration and off-flavor and that can be used in chilled beverages and ice creams.

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides a process for preparing frozen custard apple pulp or spray dried custard apple powder free from bitterness, discoloration, and off-flavor, said process comprising of (a) ripening of mature custard apple fruits at 25 - 28°C to obtain sweet and flavored pulp, (b) scooping of pulp and separation of peel to exclude the grit cells, (c) passing through a pulper to obtain pulp, free of seeds (d) thorough mixing of pulp with 0.1% ascorbic acid (w/w), (e) immediate packing of pulp in 150 - 300 guage polyethylene bags after expelling air in unit packs, (f) sealing of polyethylene bags, (g) blast freezing the pulp in polyethylene bags and immediate storage at –20 to -30°C, (h) to obtain a frozen product that can have storage life of 12 months, free of discoloration, off-flavor and bitterness, when used for consumption, after thawing at room temperature, (i) mixing 50 to 60% by weight of the pulp thus obtained in step (b) or step (c) with 5 to 10 % by weight of milk powder, 5 to 10% by weight of sugar candy and 3-10% by weight of maltodextrin, 0.7 to 3.0% by weight of tricalcium phosphate, 1 to 3% by weight of honey and the remaining being water to bring the total soluble solids in the range of 35 to 40°Brix, and (j) spray drying the mixture of step (c) at an inlet temperature in the range of 100 to 140°C and an outlet temperature in the range of 70 to 110°C to obtain spray dried custard apple powder.

DETAILED DESCRIPTION OF THE INVENTION:

Accordingly, the present invention provides a process for preparing frozen custard apple pulp or spray dried custard apple powder free from bitterness, discoloration, and off-flavor, said process comprising the steps of:

a. obtaining custard apple pulp;
b. mixing the pulp with 0.05 to 0.15% by weight of ascorbic acid;
c. optionally filling the mixture of step (b) in containers and blast freezing the same at temperature in the range of -10^{o} to -50^{o} C followed by immediately storing the

same at –15° C to –45° C to obtain frozen custard apple pulp;

d. mixing 50 to 60% by weight of the pulp thus obtained in step (b) or step (c) with 5 to 10 % by weight of milk powder, 5 to 10% by weight of sugar candy and 3-10% by weight of maltodextrin, 0.7 to 3.0% by weight of tricalcium phosphate, 1 to 3% by weight of honey and the remaining being water to bring the total soluble solids in the range of 35 to 40°Brix, and

e. spray drying the mixture of step (c) at an inlet temperature in the range of 100 to 140°C and an outlet temperature in the range of 70 to 110°C to obtain spray dried custard apple powder.

In an embodiment of the present invention, the custard apple pulp is obtained from fresh ripe custard apple fruits.

In another embodiment of the present invention, the custard apple pulp is obtained by scooping the pulp from ripe fruits using a pulper followed by separating seeds from the same.

In yet another embodiment of the present invention, wherein in step (b), 0.1% by weight of ascorbic acid is mixed with the custard apple pulp.

In still another embodiment of the present invention, wherein the mixture obtained in step (c) is fast packed in polyethylene bags and sealed after expelling air.

In one more embodiment of the present invention, the sealed containers are blast freezed at temperature in the range of -20 degree C to -30 degree C.

In one another embodiment of the present invention, the frozen pulp is stored immediately at -20 degree C to -30 degree C.

In a further embodiment of the present invention, wherein in step (d), water is added to the mixture of step (d) to bring the total soluble solids to 38°Brix.

In a further more embodiment of the present invention, wherein prior to step (e), the mixture of step (d) is filtered through a fine sieve having mesh size in the range of 36 to 52.

In an embodiment of the present invention, wherein in step (e), the mixture of step (d) is spray dried at a flow rate of 40 to 80 ml/minute.

In another embodiment of the present invention, the freeze dried custard apple pulp thus obtained has a shelf life greater than about 12 months.

Accordingly, the present invention provides a process for preparing frozen custard apple pulp or spray dried custard apple powder free from bitterness, discoloration, and off-flavor,

said process comprising of (a) ripening of mature custard apple fruits at 25 - 28°C to obtain sweet and flavored pulp, (b) scooping of pulp and separation of peel to exclude the grit cells, (c) passing through a pulper to obtain pulp, free of seeds (d) thorough mixing of pulp with 0.1% ascorbic acid (w/w), (e) immediate packing of pulp in 150 - 300 guage polyethylene bags after expelling air in unit packs, (f) sealing of polyethylene bags, (g) blast freezing the pulp in polyethylene bags and immediate storage at –20 to -30°C, (h) to obtain a frozen product that can have storage life of 12 months, free of discoloration, off-flavor and bitterness, when used for consumption, after thawing at room temperature, (i) mixing 50 to 60% by weight of the pulp thus obtained in step (b) or step (c) with 5 to 10 % by weight of milk powder, 5 to 10% by weight of sugar candy and 3-10% by weight of maltodextrin, 0.7 to 3.0% by weight of tricalcium phosphate, 1 to 3% by weight of honey and the remaining being water to bring the total soluble solids in the range of 35 to 40°Brix, and (j) spray drying the mixture of step (c) at an inlet temperature in the range of 100 to 140°C and an outlet temperature in the range of 70 to 110°C to obtain spray dried custard apple powder.

The following examples are given by way of illustration of the present invention and its use for preparation of pulp or powder from custard apple, and therefore should not be construed to limit the scope of the present invention.

EXAMPLE - 1

The process entails selection of one hundred kg of mature custard apple fruits of specific gravity ~ 1, after ripening at 25 - 28°C, is subjected to separation of pulp from peel by scooping. Seeds from pulp is separated, after passing through a pulper. After mixing pulp with ascorbic acid @ 0.1% (w/w), the pulp is packed in 150 - 300 guage polyethylene (30 x 20 cm) bags, in 1 kg amounts, sealed. The packed pulp is immediately subjected to blast freezing to obtain pulp in uniform frozen state, at -20°C. The blast frozen pulp is immediately transferred for storage at -20 to -30°C. Throughout the process operations, for all washing purpose, potable water is used.

EXAMPLE-2

Pulp obtained from custard apple fruits procured from tropical and sub-tropical belts was used for frozen storage. Pulp from fruits of tropical climate were more sweet and flavored than sub-tropical lot. Both the lots, however, responded similarly to the storage life and storage quality, the operations detailed in experimental section.

EXAMPLE - 3

Pulp was subjected to blast freezing in 200, 500 and 1000 g quantities, before storing at -20 to -30°C. All the categories retained similar storage quality at the end of 12 months.

EXAMPLE-4

The process entails extraction of pulp from mature ripe fruits by scooping and the seeds are separated using a pulper. The pulp (50%), is supplemented with milk powder (7%), sugar candy (7%) and maltodextrin (5%), tricalcium phosphate (1%) and honey (2%), on the basis of pulp weight. The supplemented pulp is diluted with water to final total soluble solids of 38°Brix, and passed through fine sieve. The entire feed material is then subjected to spray drying with an inlet temperature of 130°C that results in an outlet temperature of 100°C. The flow rate maintained at 70 ml per minute. The powder is collected and packed in airtight containers or sealed in unit laminated aluminum foil pouches.

EXAMPLE - 5

Pulp obtained from the mature ripe custard apple fruits was subjected to the preparation of spray dried powder. Pulp at 50% strength, was supplemented with milk powder (7%), sugar candy (7%), maltodextrin (5%), tricalcium phosphate (1%) and honey (2%), after diluting to a total soluble solids of 38°Brix was subjected to spray drying at an inlet temperature of 130°C with an outlet temperature of 100°C with a flow rate of 70 ml per minute. The powder tasted good when used in chilled RTS beverages/ fruit based products.

EXAMPLE - 6

In this example, pulp from custard apple fruits procured from sub-tropical climate was subjected to spray drying. Other conditions were similar as in example 1. The powder was acceptable.

The novelty of the invention is as follows:

The process involves scooping of pulp from the peel with careful exclusion of grit cells. Immediate packing of de-seeded pulp in unit packs of polyethylene bags, followed by expelling of air and sealing, subject to fast freezing in a blast freezer serve to provide a shelf-stable frozen pulp with no change in viscosity.

The product is of organic quality. The process yields a microbiologically safe product, despite the long storage life, under the storage conditions specified. The frozen pulp when subjected to use in different forms as nectar, RTS etc., is similar to fresh pulp, free of problems of discoloration, development of bitterness and off-flavor.

Novelty of the invention shrouds around conditioning the supplementation of the custard apple pulp and operating the spray dried equipment, eventually to result in a free flowing product, that is free of bitterness, off-flavor and discoloration, particularly whilst used for consumption in chilled liquid or semisolid forms. As such no product is available in the market.

The main advantages of the present invention are:

1. Custard apple fruit can be stored in the form of frozen pulp for 12 months, till the beginning of the next season of fruit availability, so that any trade can proceed uninterruptedly.
2. The frozen pulp after thawing at room temperature can be used for preparation of various products, just like from the fresh fruit pulp.
3. The entire process does not involve the use of any heat or chemicals.
4. The problems imminent of processing *viz.*, development of coloration, bitterness and off-flavor are not eventual.
5. The pulp in frozen form is microbiologically safe for consumption.
6. Spray dried powder serves to preserve custard apple fruits in dry form of extended storage life.
7. The product can serve the needs of populations bereft of custard apple production and in off-seasons.
8. The product is free from the problems of bitterness, development of off-flavor and discoloration, very characteristic of custard apple when processed.
9. No such product is available in the market.
10. The product in chilled beverage / ice cream form is pleasant to taste.

We claim :

1. A process for preparing frozen custard apple pulp or spray dried custard apple powder free from bitterness, discoloration, and off-flavor, said process comprising the steps of:
   a. obtaining custard apple pulp;
   b. mixing the pulp with 0.05 to 0.15% by weight of ascorbic acid;
   c. optionally filling the mixture of step (b) in containers and blast freezing the same at temperature in the range of -10 degree C to -50 degree C followed by immediately storing the same at -15 degree C to -45 degree C to obtain frozen custard apple pulp;
   d. mixing 50 to 60% by weight of the pulp thus obtained in step (b) or step (c) with 5 to 10 % by weight of milk powder, 5 to 10% by weight of sugar candy and 3-10% by weight of maltodextrin, 0.7 to 3.0% by weight of tricalcium phosphate, 1 to 3% by weight of honey and the remaining being water to bring the total soluble solids in the range of 35 to 40°Brix, and
   e. spray drying the mixture of step (c) at an inlet temperature in the range of 100 to 140°C and an outlet temperature in the range of 70 to 110°C to obtain spray dried custard apple powder.
2. A process as claimed in claim 1, wherein the custard apple pulp is obtained from fresh ripe custard apple fruits.
3. A process as claimed in claim 2, wherein the custard apple pulp is obtained by scooping the pulp from ripe fruits using a pulper followed by separating seeds from the same.
4. A process as claimed in claim 1 wherein in step (b), 0.1% by weight of ascorbic acid is mixed with the custard apple pulp.
5. A process as claimed in claim 1 wherein the mixture obtained in step (c) is fast packed in polyethylene bags and sealed after expelling air.
6. A process as claimed in claim 1, wherein the sealed containers are blast freezed at temperature in the range of -20 degree C to -30 degree C.
7. A process as claimed in claim 1, wherein the frozen pulp is stored immediately at -20 degree C to -30 degree C.
8. A process as claimed in claim 1 wherein in step (d), water is added to the mixture of step (d) to bring the total soluble solids to 38°Brix.

9. A process as claimed in claim 1 wherein in prior to step (e), the mixture of step (d) is filtered through a fine sieve having mesh size in the range of 36 to 52.

10. A process as claimed in claim 1 wherein in step (e), the mixture of step (d) is spray dried at a flow rate of 40 to 80 ml/minute.

11. A process as claimed in claim 1 wherein the freeze dried custard apple pulp thus obtained has a shelf life greater than about 12 months.

AMENDED CLAIMS

[received by the International Bureau on 30 March 2005 (30.03.05);
original claims 1-11 replaced by new claims 1-9 (1 page).]

1. A process for preparing spray dried custard apple powder free from bitterness, discoloration, and off-flavor from custard pulp, said process comprising the steps of:
   a. obtaining custard apple pulp;
   b. mixing 50 to 60% by weight of the pulp thus obtained in step (a) with 5 to 10 % by weight of milk powder, 5 to 10% by weight of sugar candy and 3-10% by weight of maltodextrin, 0.7 to 3.0% by weight of tricalcium phosphate, 1 to 3% by weight of honey and the remaining being water to bring the total soluble solids in the range of 35 to 40°Brix, and
   c. spray drying the mixture of step (b) at an inlet temperature in the range of 100 to 140°C and an outlet temperature in the range of 70 to 110°C to obtain spray dried custard apple powder.
2. A process as claimed in claim 1, wherein the custard apple pulp is obtained from fresh ripe custard apple fruits.
3. A process as claimed in claim 2, wherein the custard apple pulp is obtained by scooping the pulp from ripe fruits using a pulper followed by separating seeds from the same.
4. A process as claimed in claim 1, wherein step (a) the pulp is optionally mixed with 0.05-0.15% by weight of ascorbic acid.
5. A process as claimed in claim 4, 0.1% by weight of ascorbic acid is mixed with the custard apple pulp.
6. A process as claimed in claim 1 wherein in step (b), water is added to bring the total soluble solids to 38°Brix.
7. A process as claimed in claim 1 wherein in prior to step (c), the mixture of step (b) is filtered through a fine sieve having mesh size in the range of 36 to 52.
8. A process as claimed in claim 1 wherein in step (c), the mixture of step (b) is spray dried at a flow rate of 40 to 80 ml/minute.
9. spray dried custard apple powder free from bitterness, discoloration, and off-flavor obtained by the process as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

IN 03/00413

A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23B A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHIKHALIKAR NINAD V ET AL: "Studies on frozen pourable custard apple (Annona squamosa L) pulp using cryoprotectants" JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE, vol. 80, no. 9, July 2000 (2000-07), pages 1339-1342, XP002293973 ISSN: 0022-5142 abstract -/-	1-7

[X] Further documents are listed in the continuation of box C. [ ] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PARDEDE E ET AL: "Control of browning during the thawing of custard apple pulp." FOOD AUSTRALIA 1994 CORRESPONDENCE (REPRINT) ADDRESS, K. A. BUCKLE, DEP. OF FOOD SCI. & TECH., UNIV. OF NEW SOUTH WALES, PO BOX 1, KENSINGTON, NSW 2033, AUSTRALIA, vol. 46, no. 5, 1994, page 205, XP008034514 cited in the application abstract	1-7
X	GAMAGE T V ET AL: "Minimal processing of custard apple (Annona atemoya) pulp." JOURNAL OF FOOD PROCESSING AND PRESERVATION 1997 5/96 GRAFTON RD., GRAFTON, AUCKLAND, NEW ZEALAND. E-MAIL T.GAMAGE(A)XTRA.CO.N2, vol. 21, no. 4, 1997, page 289, XP008034513 cited in the application abstract	1-7

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(54) Title: SPRAY-DRIED COMPOSITIONS AND THEIR USES

(57) Abstract: The present invention relates to spray dried compositions comprising one or more active ingredients dispersed in a carrier of gum Arabic in admixture with a non ionic surfactant. The compositions are particularly useful for the encapsulation of menthol and can be used to prepare chewing gums and compressed tablets.

SPRAY-DRIED COMPOSITIONS AND THEIR USES

Technical Field

The present invention relates to compositions in an encapsulated form and to a method for the preparation of said compositions.

Background

Encapsulation is a process by which one or more active ingredients are coated with, or entrapped within, another material or system. In the fragrance and flavor industries, the encapsulation of active ingredients serves to retain the aroma in a food or consumer product during storage, protects the active from undesirable interactions with the environments, particularly the food, minimizes perfume/perfume or flavor/flavor interactions, guards against either light induced reactions or oxidation, and provides a controlled release of the fragrance or flavor.

In this industry, the most common processes for producing encapsulated products are spray-drying and, to a lesser extent, extrusion and coacervation.

Spray drying is a well-known operation often employed by the flavor industry to render liquid flavors into a dry free-flowing powder form. It is a cost effective and efficient process to achieve this objective. The industry standard for the formulation consists of two major components: 80 parts of non-flavoring ingredient(s) and 20 parts of flavor, which is generally a hydrophobic liquid at room temperature. It is customary to add certain emulsifiers as part of the formulation if the non-flavoring ingredient lacks or is deficient in emulsifying properties.

In spray-dried powders, an active ingredient such as a flavor or a fragrance, usually hydrophobic, is entrapped as liquid droplets in a solidified matrix of a dehydrated carrier, generally consisting of carbohydrates, such as starches, hydrolyzed starches (maltodextrin), chemically modified starches, emulsifying polymers (gum Arabic) and in certain instances monomers and dimers of simple aldohexoses, or any combination thereof. Conventional spray-drying techniques are perfectly well documented in the prior art. See for example Spray-Drying Handbook, 4th ed., K. Masters, (1985) or other reference books on the subject-matter.

The method for the preparation of a spray-dried powder typically first comprises

the dispersion of a carrier in water, and then the mixture of this dispersion with a fragrance or flavor before homogenization to form an oil-in-water emulsion. The emulsion is then spray-dried to produce a powdered product.

The present invention deals mainly with the preparation of spray-dried hydrophobic substances wherein the matrix consists essentially of gum Arabic and the contents of the finished powder product in hydrophobic encapsulate is above 25%, more preferably above 35% by weight, relative to the weight of finished product. Such spray-dried products are known as "high-fix" products, i.e. powders where the contents in hydrophobic material or encapsulated oil are above the 20-25% value that is conventional for this type of encapsulation technology.

Gum Arabic, also known as gum acacia, is a cost-effective, highly appreciated and widely used encapsulation material for spray-dried products. Its use is compatible with the regulatory requirements for Kosher and Halal certifications. Moreover, the fact that it does not have strong taste or aroma makes it a desirable carrier for the encapsulation of a large variety of flavor materials.

The gum consists of low molecular weight polysaccharides and a small amount of hydroxyproline-rich glycoprotein and minerals. This unique chemical composition leads to some of its unique functionalities which render it desirable for spray-drying. The relatively low molecular weight polysaccharides allow the preparation of gum solutions of low viscosity at high solids content. The glycoproteins provide the useful emulsifying properties of the gum. The latter also has an ability to form continuous films, is bland in taste and shows low hygroscopicity.

Although there is an abundance of literature describing the various factors affecting spray-drying efficiency upon the use of carbohydrate polymers as carriers, when it comes to the use of gum Arabic as carrier, by itself or in combination with other carbohydrates, there is much less information in the prior art.

In a recent study, B. F. McNamee et al., J. Agric. Food Chem. 49, 3385-3388, 2001, showed that partially replacing gum Arabic with maltodextrine could improve flavor retention by increasing the feeds solids supplied to the dryer. Y. Watanabe et al., J. Agric. Food Chem. 50, 3984-3987, 2002, described the effect of acyl ascorbate on the oxidation of linoleic acid in spray-dried system using maltodextrine and gum Arabic as carrier and showed that partial replacement of the latter by the former improved the

oxidative stability of the powder. Finally, A. C. Bertolini et al., J. Agric. Food Chem. 49, 780-785, 2002, studied the oxidative degradation of monoterpenes in gum Arabic spray-dried products. All the commonly used monoterpenes tested, such as limonene, β-myrcene, β-pinene, citral and linalool, oxidized rapidly at 55 C, indicating the poor oxygen barrier properties of gum Arabic film.

It is also a known fact that there is volatile loss occurring during spray drying and that such losses increase with increasing fix levels. However, literature on high-fix spray drying is scarce.

In order to achieve high-fix levels of hydrophobic material, it is known to use special encapsulating matrices. Formulations with high fix levels, typically above 50%, can be effectively spray dried with oil retentions in excess of 90% using modified starch (Octenyl Succinylated Starch – OSS) as a carrier. This has been described for instance in US 3,971,852. This patent relates primarily to carrier systems employing an emulsifying starch (OSS) in combination with low-molecular weight carbohydrates to achieve oxidative stability in the finished product. It also describes in an example the use of gum Arabic in combination with sorbitol and di-isooctyl sulfosuccinate (an emulsifier) to obtain a spray dried powder with 57.2% (w/w) oil content.

Nevertheless, the use of di-isooctyl sulfosuccinate (ionic surfactant/emulsifier) is not always possible for food applications for regulatory reasons.

Traditionally, when gum Arabic is used as the carrier, the aroma oil fix levels in such spray drying formulations is no more than 25% by weight, relative to the weight of spray-dried product. The reason for such a limitation is the excessive loss of the oil during the spray drying process when the fix level exceeds 25%.

For example, in a recent study carried out by the present inventors, for the encapsulation of menthol, mint oils or other mint flavor compositions in gum Arabic, the results indicated that, at or near conventional oil fix levels (20%), the retention of the menthol flavor on gum the Arabic carrier was only 89% at best.

The present invention aims at providing improved products spray-dried with gum Arabic as the carrier. The products of the invention carry an amount of encapsulated hydrophobic material above 25% by weight, and more preferably of at least 35% by weight, relative to the weight of the spray-dried product, with a retention level of the oil above 90% and, most times, close to a 100%.

Summary of the Invention

The present invention now relates a novel spray-dried composition, comprising at least one active ingredient dispersed in a carrier of gum Arabic, wherein said active ingredient is present in an amount above 30% by weight, relative to the dried weight of the composition, the latter further comprising a non-ionic surfactant.

What is meant here by an "active ingredient" is a hydrophobic ingredient, to be protected by way of solid encapsulation. It may include volatile perfuming or flavoring ingredients, as well as other kinds of ingredients, namely nutritional supplements such as omega-3 and omega-6 fatty acids, vitamins or pharmaceutical actives for instance.

The invention further relates to a spray-dried composition as cited above further containing a fireproofing agent.

The invention also relates to a spray-dried composition as cited above wherein the active ingredient is menthol, a menthol-containing flavor or fragrance or a flavor or fragrance with a mint tonality. Such compositions are particularly advantageous in that they make it possible to impart to foods and other consumer products cooling and sensate properties, and to minimize irritation effects possibly associated with the organoleptic effect of menthol in particular.

The invention further relates to a method for the preparation of such a spray-dried composition, and to its use for the flavoring or perfuming of consumer products such as foods, beverages, pharmaceutical or oral care compositions, or yet perfuming compositions.

The spray-dried powder of the invention can also be advantageously used as an intermediate product or starting product for a double-encapsulation method, i.e. as a solid product susceptible of being subjected to a further encapsulation such as an extrusion in a glassy matrix to provide a granular delivery system, or to a second spray-drying operation in a distinct or similar matrix, and the invention also relates to that use of the composition.

More objects, aspects and advantages of the invention will become apparent from the detailed description hereafter.

Brief Description of the Drawings

Figure 1 represents the percentage of menthol retention in gum Arabic and

maltodextrine based spray dried products as a function of the menthol concentration.

Figure 2 represents the amount of oil (menthol) that is solvent extractable (oil not encapsulated, remaining at the surface of the spray dried product), as a function of menthol concentration.

Detailed Description of the Preferred Embodiments

The present invention thus relates to a novel spray-dried composition, comprising at least one active ingredient dispersed in a carrier of gum Arabic, wherein said active ingredient is present in an amount above 30% by weight, relative to the dried weight of the composition, the latter further comprising a non-ionic surfactant.

According to one embodiment of the invention, the emulsifier is preferably a food grade emulsifier, namely a di-acetyl tartaric acid ester of mono and diglycerides (DATEM). An example of the latter is the product commercialized under the tradename of Panodan by Danisco A/S, Langenbrogade 1, PO Box 17, Copenhagen, DK-1001.

As pointed out above, gum Arabic has very good emulsifying properties but limited emulsifying capacity. For this reason it works extremely well with respect to flavor retention when used as a carrier in spray drying. However, the performance of such a carrier can be adversely affected when an additional emulsifier/surfactant is added as part of the formulation. We have however found that the addition of a non-ionic surfactant has no detrimental effect on the spray drying of up to 50% by weight of mint flavours in gum Arabic matrices and this is a very surprising result.

The invention further relates to a composition in the form of a spray-dried powder, comprising one or more active ingredients dispersed in a carrier, wherein said carrier consists essentially of a mixture of gum Arabic with a non-ionic surfactant.

The spray-dried product of the invention turned out to be very useful for encapsulating high amounts of hydrophobic liquid ingredients useful in the perfume and flavor industry, in particular for obtaining powders of menthol and mint flavours or fragrances containing up 45% by weight of menthol, relative to the weight of the powder products. Such menthol, mint oils or other mint flavor composition powders are of very great importance for use in oral care products in particular, chewing gums and tablets for example, wherein the high concentration renders the use of the spray-dried mint flavor particularly cost-effective in application. They are also particularly useful for perfumed

applications such as foaming shaving oils and antiperspirants.

The compositions of the invention prevent excessive oil loss during the spray-drying process, make it possible to obtain concentrations in active ingredients which are close to 50%, with a retention of nearly 100% during the common shelf-life periods, and this using carriers which fulfil wide regulatory criteria, namely for food products.

According to an embodiment of the invention the composition contains at least 0.5% by weight of non-ionic emulsifier and between 30 and 50% by weight of active ingredient, relative to the weight of the composition.

Following an even more advantageous embodiment, the compositions will comprise from 2 to 10% by weight of emulsifier and at least 40% of active encapsulate, the remainder of the composition being gum Arabic.

Following a best embodiment of the invention there is provided a spray-dried composition consisting of 55 to 60% by weight of gum Arabic, 2 to 5% of DATEM and the remainder being menthol or a mint active composition, namely a mint flavor.

In the compositions of the invention there can be used any gum Arabic available commercially, under any one of its common names such as Turkey gum, Indian gum, Acacia Senegal, Gum #414 or gum Arabic. The nature and origin of the gum is not an essential parameter of the invention.

The essential characteristic of the invention thus resides in the combination of the gum Arabic with the non-ionic emulsifier, more particularly a DATEM. Other non-ionic emulsifiers that have proved appropriate according to the invention include Tween 80 (polyoxyethylesorbitan monooleate; commercialised by Uniquema, 3411 Silverside Road, Wilmington, DE 19803) and Glycosperse L20-K (polyoxyethylenesorbitan monolaurate; [commercialised by Lonza Inc., 90 Boroline Road, Allendale, NJ 07401]).

As the active encapsulate, there can be used any liquid hydrophobic ingredient that one desires to obtain in powder form. The compositions of the invention are in fact valuable for producing highly concentrated, free flowing powders, soluble in aqueous systems so as to release the active ingredient.

According to very useful embodiments of the invention, the active ingredient dispersed in the carrier of the spray-dried composition of the invention will preferably be a hydrophobic flavor or fragrance ingredient or composition of current use.

The terms "flavor and fragrance ingredient or composition" as used herein are

deemed to define a variety of flavor and fragrance materials of both natural and synthetic origin. They include single compounds and mixtures. The composition of the invention can encapsulate volatile or labile components in liquid form, preferably hydrophobic. Specific examples of such components may be found in the current literature, e.g. in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M.B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA), as well as in the vast published and patent literature relating to the fragrance and flavor industrie's technical developments. These substances are well known to the person skilled in the art of perfuming, flavoring, and/or aromatizing consumer products, i.e. of imparting an odor and/or a flavor or taste to a consumer product traditionally perfumed or flavored, or of modifying the odor and/or taste of said consumer product.

Natural extracts can also be encapsulated into the system of the invention; these include e.g. citrus extracts such as lemon, orange, lime, grapefruit or mandarin oils, or coffee, tea, mint, cocoa, vanilla or essential oils of herbs and spices, amongst other. As previously mentioned, a preferred application relates to the encapsulation of mint oils.

Other ingredients that can be preferentially encapsulated according to the invention relate to nutritional ingredients such as animal or vegetable oils containing high amounts of omega-3 and and/or omega-6 fatty acids, namely fish oils.

Another object of the invention is a method for the preparation of a spray-dried powder, which comprises the steps of emulsifying the active ingredient in the gum Arabic and non-ionic emulsifier mixture; homogenizing the emulsion and spray drying the latter to form a particulate product.

One particular advantage of the process according to the invention lies in the fact that the compositions comprising a combination of gum Arabic with non-ionic emulsifier, as here-described, demonstrate a retention of the active ingredient (oil) which is advantageously not affected by a variation in the solid content of the starting aqueous emulsion. More particularly, in classical spray-drying processes, a high dilution rate, useful to provide mono-dispersity of the gum powder, must be balanced with the fact that the higher is the dilution rate, the lower will be the capability of the carrier film (after spray-drying) to retain the active oil, namely the flavor or fragrance. It is furthermore established that a solid content below 10% in the initial aqueous emulsion is expected to

result in a noticeably decreasing active ingredient retention after spray-drying. Now, it turned out in the present case that, as shown in the examples below, the active hydrophobic encapsulate retention of the product of the invention is not affected by the dilution rate, or solid content in the aqueous emulsion introduced into the spray-drier. In other words, high dilution rates may be employed in order to get a good mono-dispersity of the carrier powder without provoking any drawback on the encapsulated oil retention, which is a totally unexpected result.

The spray-drying apparatus used in the process of the invention can be any one of the various commercially available apparatuses. Examples of spray-drying apparatuses are the Anhydro Dryers (origin: Anhydro Corp. of Attleboro Falls, Mass.), the Niro Dryer (manufactured by Niro Atomizer Ltd., Copenhagen, Denmark), or a Leaflash apparatus (origin : CCM Sulzer). Preferably a spray-drier with a pressure nozzle is used.

The process will be described in a more detailed manner in Example 1. However, the typical parameters of a spray-drying process are well known in the art and can be easily adjusted by a skilled person in the art.

The particles of the invention have typically a size comprised between 50 and 70 μm and a bulk density comprised between 0.4 and 0.6 g/cm^3. However, the granulometry and the bulk density of the resulting dry powders can be adjusted by selecting the nozzle (orifice size/diameter) and the atomization pressure so as to obtain the desired powder flowability.

The spray-dried powders prepared according to a process of the invention can be utilized as such in applications, for instance for the perfuming or flavoring of compositions wherein release is induced by contact with water or a source of humidity such as sweat, in perfumery applications, or saliva in the context of food intake or chewing tablets or gum. The products can be used cost effectively in any application where eventual water solubility of the carrier is desired resulting in the release of the active component.

One typical and very useful application is in the preparation of chewable tablets. In such tablet applications, upon the production of the tablets, a free-flowing flavor composition is critical when high-speed machines are employed. Yet, it is known that classical high-fix powders tend to be less free flowing than their low-fix counterparts primarily due to the un-encapsulated oil (solvent extractable oil) on the surface of the

particle. The formulations of the invention result in low solvent extractable oil and thus yield a very free-flowing product with high flavor retention at high fix levels. This renders them particulary valuable when used in high-speed machines for portion packaging or tablet making.

The spray-dried compositions of the invention can also be advantageously used as starting materials to be subjected to further processing, before being used as delivery systems in a variety of applications.

In particular, in one embodiment of the invention, the spray-dried particles obtained by the method here-above described, can be further encapsulated in an extruded glassy matrix which may be formed from one or more carbohydrate materials or which may just comprise a plasticizer and an emulsifying agent, in order to produce a glassy matrix with an improved thermal stability. US 5,087,461, the contents of which are hereby included by reference, discloses an encapsulation method of a spray-dried composition by way of extrusion. This process leads to narrow rods having a diameter in the range of 0.3 to 3 mm.

Apart from the extrusion, other kinds of encapsulation processing, following the spray-drying, are possible. The powder obtained can for instance be submitted to a second spray-drying, thus providing a two-stage spray-dried product. This technique in particular, as well as multi-stage spray-drying in general, are described by W.J. Coumans, P.J.A.M. Kerkhof and S. Bruin in Drying Technology, Vol. 12 (1 and 2), (1994), the teaching of which is hereby included by reference.

These examples are not restrictive of the encapsulation techniques which can be used for further processing of the spray-dried powder obtained according to the present invention, notably with the aim of increasing the size of the particles, or improving a particular characteristic of the powder, in order to rend it suitable for specific applications.

The compositions of the invention may also contain optional ingredients in addition to the gum Arabic carrier, the non-ionic emulsifier and the hydrophobic active ingredient. According to particularly useful embodiments, they further contain an effective amount of a fireproofing or explosion suppression agent susceptible of reducing the violence of powder explosion. The type and concentration of such agents in spray-drying compositions has been disclosed in detail in WO 03/043728 A1 (FIRMENICH), the

contents of which are hereby included by reference. This document discloses perfuming or flavouring microcapsules having fireproofing agents dispersed in or absorbed within a polymeric carrier material, the fireproofing agents being basically inorganic salts. Reference is specifically made here to the teachings and examples in this document as they relate to the citation of the specific agents that can be used in the context of the present invention, the processes for their incorporation into the compositions of the invention and the typical concentrations for their use.

Other agents suitable as explosion suppressants, apart from those described in WO 03/043728, also possibly having further beneficial properties, are also contemplated according to the invention. They may for example be usable in smaller amounts, have a beneficial effect on the hygroscopicity of the microcapsules, or yet be particularly suitable for use in food applications.

For example, C_1-C_{12} carboxylic acids, salts of C_1-C_{12} carboxylic acids, and mixtures thereof can be directly added to perfuming and flavouring microcapsules in an amount effective to reduce the violence of possible explosions during their preparation, in particular when suspended in hot air, and during their storage.

The term "C_1-C_{12} carboxylic acids" refers here to carboxylic acids containing 1 to 12 carbon atoms, including the C-atom of the carboxyl group. Therefore, if more than one carboxylic group is present in the carboxylic acid, the carbon of each carboxylic group shall be counted in the total number of carbon atoms mentioned.

The carboxylic acids and/or their salts possibly used as explosion suppressants in microcapsules of the present invention may be linear, branched, cyclic, and/or aromatic carboxylic acids and/or their salts. The carboxylic acids may be saturated or unsatured hydrocarbons.

Examples of cyclic carboxylic acids are lactones, for example ascorbic acid is a preferred such explosion suppression agent. An example of an appropriate aromatic carboxylic acid is salicylic acid.

Preferably, the carboxylic acids and/or their salts are functionalised hydrocarbon carboxylic acids and/or their salts.

Preferably, the carboxylic acid comprise less than 7, more preferably less than 5 and most preferably less than 3 carbon atoms covalently bound to 2 hydrogen atoms.

Preferably, the carboxylic acid of the present invention comprises 5 or less carbon

atoms with an oxidation number of (–II) or more negative. More preferably, the carboxylic acid comprises 3 or less carbon atoms having a oxidation number of (-II) or more negative.

In an embodiment of the present invention, the carboxylic acids and/or their salts are hydroxy- and/or ceto-functionalised hydrocarbon carboxylic acids and/or their salts.

Preferably, the carboxylic acid of the present invention comprises at least 1 hydroxy group. Preferably, it comprises at least 2 hydroxy groups.

In a further embodiment of the microcapsules of the present invention, the carboxylic acids and/or their salts are di-, tri-, or multi carboxylic acids and/or their salts. Examples of multi carboxylic acids include citric acid, which is C_6-tricarboxylic acid.

Preferably, the carboxylic acid is at least a di carboxylic acid. More preferably, it is at least a tri carboxylic acid, meaning that it carries at least three carboxylic groups.

Preferably, the carboxylic acid and/or their salt is a C_4-C_8 carboxylic acid and/or their salt.

In a preferred embodiment of the present invention, the carboxylic acid and/or their salts are selected from C_2-C_6 carboxylic acids and/or their salts.

In preferred modes of carrying out the invention, the carboxylic acid and/or its salt is selected from the group consisting of acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, citric acid, succinic acid, hydroxysuccinic acid, maleic acid, fumaric acid, oxylic acid, glyoxylic acid, adipic acid, lactic acid, tartaric acid, salicylic acid, ascorbic acid, the potassium, calcium and/or sodium salts of any of the afore-mentioned acids, and mixtures of any of these.

Preferably, the salts of the carboxylic acids are potassium and/or sodium salts. More preferably, there shall be used the tri-potassium and/or trisodium salt of a tri-carboxylic acid. Most preferably, it is the tripotassium and/or trisodium salt of citric acid.

The above acids and their salts are commercially available. They can also be synthesized or extracted from natural materials by methods known per se.

Typically, the capsules will comprise from 2 to 15%, more preferably 2 to 10%, by weight of explosion suppressant, relative to the dry weight of the microcapsules.

The explosion suppressant can be added to the aqueous emulsion consisting of the perfuming or flavouring ingredient dispersed in the gum Arabic and non-ionic emulsifier. The obtained emulsion is then spray-dried in order to form the powder. This

encapsulation technique does not require a more detailed description herein, as it relies on the conventional spray-drying techniques already mentioned earlier and which are perfectly well documented in the prior art [see for example Spray-Drying Handbook, 3rd ed., K. Masters ; John Wiley (1979)] and currently applied in the food industry or in the flavour and perfume industries.

In another embodiment, the explosion suppressant, in the form of a solid powder, is simply blended with the spray-dried powder prior obtained as described earlier from the aqueous emulsion of the hydrophobic aqueous ingredient or composition in the gum Arabic carrier and the non-ionic emulsifier.

The products of the invention, namely the spray-dried powder as such, as well as the spray-dried compositions further subjected to a second kind of encapsulation can be advantageously used for instance for the perfuming or flavoring of food compositions in particular.

Therefore, the delivery systems of the invention can be used in applications such as chewing gums or chewing sweets, chewing tablets, savory food or baking in the field of flavors. Similarly the field of perfumery comprises many applications where this kind of encapsulation systems may be very useful, particularly for detergents in tablet form, for foaming shaving oils and for antiperspirant sprays, powders and sticks.

The concentrations in which the microcapsules of the invention can be incorporated in the consumer products vary in a wide range of values, which are dependent on the nature of the product to be perfumed or flavoured. Typical concentrations, to be taken strictly by way of example, are comprised in a range of values as wide as from a few ppm up to 5 or 10% of the weight of the flavoring or perfuming composition or finished consumer product into which they are included.

The high-fix products of the invention, especially those having up to 50% weight content in active ingredient, prepared using gum Arabic in combination with a non-ionic surfactant/emulsifier, have substantially improved active ingredient, namely flavor, retention compared to their counterparts prepared using maltodextrins as carriers. They also yield powders with relatively low solvent extractable oil indicating efficient encapsulation especially at high active ingredient, in particular flavor, retention levels >95%). Some of the formulations and the analytical results are given below in the Examples.

The invention will now be described in a more detailed manner in the examples below, wherein the temperatures are indicated in degrees Celsius and the abbreviations have the usual meaning in the art.

Examples

The following examples are further illustrative of the present invention embodiments, and further demonstrate the advantages of the invention devices relative to prior art teachings.

Examples 1-9

Preparation of spray-dried compositions according to the invention and comparison with maltodextrine containing compositions

Nine powder formulations were prepared using the materials, equipment and general method conditions described hereafter.

Materials:

Carrier:	Gum Arabic
	Maltodextrin Morex 10-18 DE
Emulsifier:	Panodan - FDPK DATEM of soybean oil origin
	Lamegin 39665 DWPS Cognis - DATEM of Sunflower oil origin
	Tween 80K
	Glycosperse L020K (Sorbitan Monococoate)
Flavor:	Menthol

Equipment: Spray Dryer (box type) with nominal water evaporation rate of 60 kg/hr
Two-Stage homogenizer high-pressure pump
Clevenger Continuous Steam Distillation Apparatus
Gas Chromatograph - Hewlett Packard

Powder formulation:

TABLE 1

Sample #	% Ingredient					
	Gum Arabic	Maltodextrin	Menthol	DATEM	Tween 80	Glycosperse L20-K
1	58.00	--	40.00	2.00	--	--
2	47.50	--	50.00	2.50	--	--
3	37.00	--	60.00	3.00	--	--
4*	--	58.00	40.00	2.00	--	--
5*	--	47.50	50.00	2.50	--	--
6*	--	37.00	60.00	3.00	--	--
7	58.00	--	40.00	--	2.00	--
8	58.00	--	40.00	--	--	2.00
9	55.00	--	42.00	3.00	--	--

* Comparison samples, using maltodextrine as the carrier

Spray Drying Method:

The spray drying conditions were as given below:

Feed Solids = 40% (non aqueous matter)

Feed Temperature = 65°C

Homogenization Pressure = 100 bars

Feed Pressure = 170 - 200 bars

Dryer Inlet Temperature = 175°C

Dryer Outlet Temperature = 80°C

Dryer Air Flow Rate = 30 meter^3/minute

Spray Nozzle = 70/216 supplied by Spraying Systems Inc.

Samples were collected and analyzed as follows:

Total Oil Determination: Total oil was determined by continuous steam distillation, using the Clevenger apparatus, using a 10 g sample. One ml of toluene was added to the distillation flask to prevent crystallization of menthol in the side arm of the assembly. Distillation was done for two hours. Oil content was calculated by the following formula:

Gravimetric oil content = [(ml Oil-1) x 0.89[a]] / [sample weight g]

[a] Density of menthol

Solvent Extractable Oil: A GC-Internal Standard method described in literature by A. Scottitantawat et al, in J. Food Sci., Vol 68, No.7, **2003**, p. 2256-2261, was modified and used. Extraction time was reduced to 10 seconds and 2-nonanone was used as an internal standard.

Table 2 summarizes the analytical results of the nine spray-dried menthol samples prepared by the method above with the respective materials indicated in Table 1.

TABLE 2

Sample #	% Fix	% Oil content	% Retention	Extractable oil %
1	40.00	40.05	> 100.00	0.75
2	50.00	48.06	96.12	5.52
3	60.00	56.07	93.45	29.40
4*	40.00	37.38	94.50	3.70
5*	50.00	35.60	71.20	7.50
6*	60.00	44.50	74.17	8.20
7	40.00	41.83	> 100.00	0.08
8	40.00	39.60	99.00	0.04
9	42.00	40.50	96.43	--

* Comparison samples, using maltodextrine as the carrier

The results in this Table show clearly that the carrier system used in spray drying has a significant impact on menthol retention as well as the solvent extractable flavor/oil, gum Arabic showing consistent superiority, when compared to maltodextrin, both in its ability to to retain the oil, over a wide range of concentrations, and in the capability of reducing the level of solvent extractable oil for concentrations of encapsulated oil below 50% by weight. These effects are depicted graphically in Figures 1 and 2 respectively.

Solvent extractable oil is considered as un-encapsulated in dry powders. If the solvent extractable menthol was calculated as a percentage of total menthol in the powder it would suggest a very high (>98%) encapsulation. However, with increasing fix levels the amount of solvent extractable oil increases dramatically when the emulsifier is used at 5% level based on the menthol content and gum arabic is used as a carrier.

When using maltodextrin as carrier with the same emulsifier, the flavor loss is very pronounced when the fix level exceeds 40%, although the increase in solvent extractable oil is not very significant.

Example 10

Preparation of spray-dried compositions according to the invention, with different solids content

Proceeding as indicated in the preceding examples, there were prepared samples of encapsulated oils according to the invention, having the same dry weight composition as that of sample 1 in Table 2, by varying the feed solids weight percentage used in the process. The results of these tests are given here-below.

Sample	% Solvent Extractable oil	Feed solids (% non-aqueous matter)	% Retention
A	0.037	20	97.90
B	0.037	30	99.03
C	0.057	50	99.03

The above results show that varying the solid content of the starting emulsion, in the process of the invention, does not affect the retention of encapsulated oil.

Example 11

Preparation of a foaming shaving oil

A foaming shaving oil, perfumed via the use of the invention's gum Arabic capsules encapsulating a perfume, was prepared by admixing, in a generally known manner, the following ingredients.

Ingredients	% by weight
Isopropyl palmitate	49.00
Trilaureth-4 phosphate	2.00
MIPA-laureth sulfate (and) laureth-4 (and) cocamide DEA	42.30
Sunflowerseed amidopropyl	0.50
Dimethylamine lactate bisabolol	0.50
Cocamide DEA	3.00
KATHON CG (Rohm & Haas)	0.10
Tocopherol (TENOX GT-2, Eastmann)	0.50
Dilauryl thiodipropionate	0.10
Perfume	1.00
Gum Arabic capsules	1.00

Example 12

Preparation of an antiperspirant spray

An antiperspirant spray, perfumed via the use of the invention's gum Arabic capsules encapsulating a perfume, was prepared by admixing, in a generally known manner, the following ingredients.

Ingredients	% by weight
Cyclomethicone	11.75
Isopropyl myristate	2.20
Silica	0.25

Quartenium-18 Hectorite	0.80
Aluminium chlorohydrate	8.00
Perfume	0.40
Gum Arabic capsules	1.60
Propane/Butane 2.5 bar	75.00

Example 13

Preparation of an antiperspirant powder

An antiperspirant powder, perfumed with the invention's gum Arabic capsules encapsulating a perfume, was prepared by admixing, in a generally known manner, the following ingredients.

Ingredients	% by weight
Talcum	87.00
Aluminium chlorohydrate	10.00
Perfume	1.50
Gum Arabic capsules	1.50

Example 14

Preparation of an antiperspirant stick

An antiperspirant stick, perfumed via the use of the invention's gum Arabic capsules encapsulating a perfume, was prepared by admixing, in a generally known manner, the following ingredients.

Ingredients	% by weight
Cyclomethicone	48.50
Steraryl alcohol	21.00
PPG-14 Butyl ether	2.00

Hydrogenated Caster oil	1.00
Octyldodecanol	4.00
Aluminium chlorohydrate	21.00
Perfume	1.00
Gum Arabic capsules	1.50

Example 15

Preparation of a chewing gum

A chewing gum, flavored via the use of the invention's gum Arabic capsules encapsulating a flavor, was prepared by admixing, in a generally known manner, the following ingredients.

Ingredients	% by weight
Confectioners sugar	59.35
Gum Base-Nova Base T	19.40
Corn syrup, 42 DE	19.80
Citric acid	0.70
Glycerine	0.50
Gum Arabic capsules	0.25

Claims

1. A spray-dried composition, comprising at least one active ingredient dispersed in a carrier of gum Arabic, wherein said active ingredient is present in an amount above 30% by weight, relative to the dried weight of the composition, the latter further comprising a non-ionic surfactant.

2. A spray-dried composition according to claim 1, wherein the non-ionic surfactant is a di-acetyl tartaric acid ester of mono- or di-glycerides.

3. A spray-dried composition according to claim 2, wherein the active ingredient is a flavor or a fragrance ingredient or composition.

4. A spray-dried composition according to claim 3, wherein the active ingredient is menthol, mint oil or a mint flavor.

5. A spray-dried composition according to claim 1, comprising 2 to 15% by weight of a non-ionic surfactant selected from the group consisting of the di-acetyl tartaric acid esters of mono- and di-glycerides, polyoxyethylenesorbitan monooleate and polyoxyethylenesorbitan monolaurate type surfactants, relative to the dried weight of the composition.

6. A spray-dried composition according to claim 1, which comprises from 30 to 50% by weight of active ingredient, relative to the dried weight of the composition.

7. A spray-dried composition according to claim 6, comprising menthol, mint oil or a mint flavor and wherein the non-ionic surfactant is a di-acetyl tartaric acid ester of mono- or di-glycerides

8. A spray-dried composition according to claim 7, wherein the non-ionic surfactant is present in a concentration comprised between 2 and 10% by weight, relative to the dried weight of the composition.

9. A spray-dried composition according to claim 1, which further comprises an explosion suppression agent.

10. A spray-dried composition according to claim 9, wherein the explosion suppression agent is selected from the group consisting of sodium silicate, potassium silicate, sodium carbonate, sodium hydrogencarbonate, monoammonium phosphate or carbonate, diammonium phosphate, mono-, di- or trisodium phosphate, sodium hypophosphite, melamine cyanurate, chlorinated hydrocarbons and mixtures thereof.

11. A spray-dried composition according to claim 10, wherein the explosion suppression agent is selected from the group consisting of acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, citric acid, succinic acid, hydroxysuccinic acid, maleic acid, fumaric acid, oxylic acid, glyoxylic acid, adipic acid, lactic acid, lactic acid, tartric acid, salicylic acid, ascorbic acid, the potassium, calcium and/or sodium salts of any of the afore-mentioned acids, and mixtures of any of these.

12. A spray-dried composition according to claim 10, comprising from 5 to 15% by weight of explosion suppression agent, relative to the dried weight of the composition.

13. A spray-dried composition according to claim 11, comprising from 5 to 15% by weight of explosion suppression agent, relative to the dried weight of the composition.

14. A product consisting of a food, a beverage, a nutrition supplement, an oral care composition, a deodorant, a tablet or a chewing gum, which comprises a spray-dried composition according to claim 1 in an amount sufficient to impart, improve, modify or enhance the taste , odor and/or nutritional value thereof.

15. A product according to claim 14, in the form of a chewing tablet or gum.

16. A product according to claim 14, in the form of a soap or detergent tablet or of a body deodorant or foam shaving oil.

17. A method for flavoring, perfuming and/or fortifying a product which is a food, a beverage, a nutrition supplement, an oral care composition, a tablet or a chewing gum, a soap or detergent tablet or a body deodorant or foam shaving oil, which comprises adding a spray-dried composition according to claim 1 thereto, in an amount sufficient to impart, improve, modify or enhance the taste, odor and/or nutritional value of said product.

18. A method according to claim 17, wherein the product is a chewing tablet or gum.

19. A method according to claim 17, wherein the product is a soap or detergent tablet, a spray, powder or stick antiperspirant, or a foaming shaving oil.

FIGURE 1 - Menthol retention for gum arabic and maltodextrin

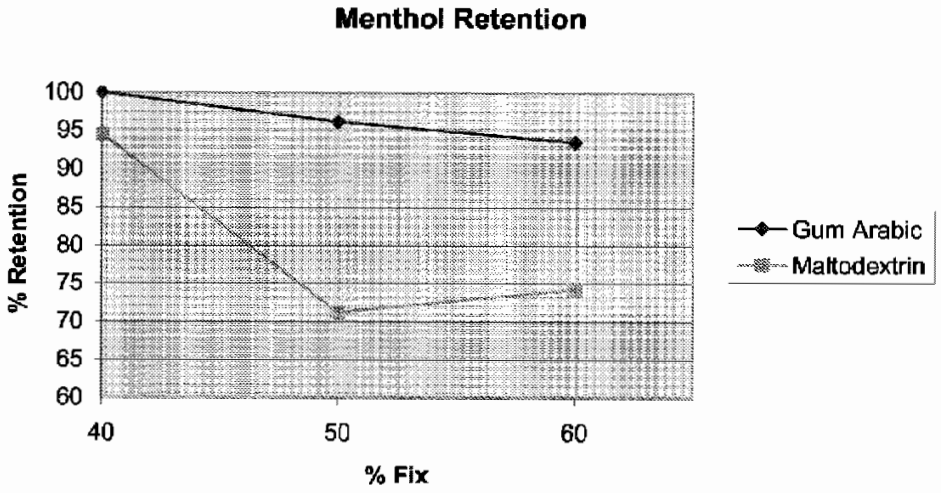
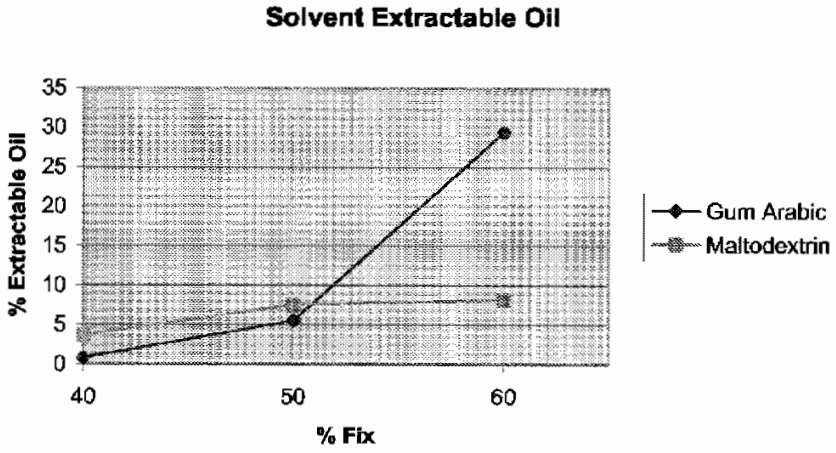


FIGURE 2 - Solvent extractable oil content



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/22 A23G4/00 A61K9/16 C11B9/00 A61K8/11
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 173 838 A (BROOKS GARY) 16 March 1965 (1965-03-16) claim 3; example 4 column 8, paragraph 4	1,2,5,6, 8,14,17
Y		3,4,7, 9-13,15, 16,18,19
Y	US 3 971 852 A (BRENNER ET AL) 27 July 1976 (1976-07-27) cited in the application column 9, line 4 - line 5 example 2 column 16, line 65 - column 17, line 62	3,4,7, 15,16, 18,19

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/043728 A (FIRMENICH SA; HOLZNER, GUENTER; MOSER, ANDRE) 30 May 2003 (2003-05-30) cited in the application claims; examples	9-13

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2006/050225

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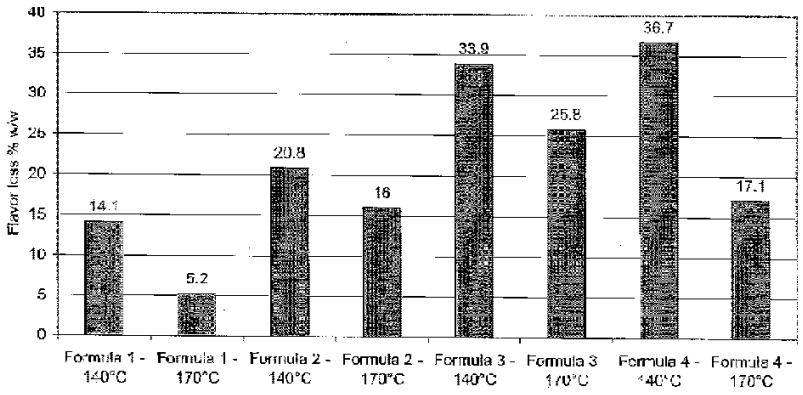
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(54) Title: FLAVOUR AND/OR FRAGRANCE CAPSULES



(57) Abstract: The present invention relates to capsules encapsulating a flavour and/or fragrance ingredient, the capsules being obtainable by a method in which an emulsion comprising the ingredient is dispersed in the form of drops in a spraying tower and exposed to a temperature in the range of 121 to 250°C. In the tower, a cloud of suspended powdering agent provides a coating and prevents the capsules from sticking together. The capsules have a high ingredient load of about 18-40 wt.% and a particle size in the range of 100 to 2000 µm. The method for obtaining the capsules has the advantage of substantially less loss of ingredient during drying if compared to similar processes of the prior art.

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Flavour and/or Fragrance Capsules

Technical Field

The present invention relates to a method for preparing capsules having an average diameter in the range of 100 to 2000 µm, more particularly from 200 to 800 micron, and encapsulating a flavor and/or fragrance ingredient. The invention further relates to capsules as such, a method for reducing loss of ingredients during preparation of the capsules and the use of a multi stage drying apparatus for preparing capsules of the invention.

Background of the Invention and Problem to be Solved

The objective of the present invention is the encapsulation of flavour and/or fragrance compounds and/or compositions in particles having an average diameter of 100 to 2000 µm and more particularly 200 to 800 µm. Encapsulation, in general, has the purpose of providing a stable and transportable form of an active ingredient. If the active ingredient is liquid at ambient temperature, encapsulation within particles has the further advantage of providing easier handling and mixing with dry products and a less concentrated form of the active ingredient, the latter being an advantage in some instances

Encapsulation of active ingredients in free flowing powders also generally has the purpose of creating a form of active ingredients that can conveniently be dosed and mixed with other ingredients or be directly added to consumer end products. In this regard, particle size and load of active ingredient become relevant. Relatively large particles become useless if small quantities of active ingredient are to be added to a consumer end product, because the fluctuations of final concentration of the active ingredient may become quite considerable. Relatively small particles, on the other hand, suffer from a less beneficial surface to volume ratio. This ratio is particularly relevant with volatile active ingredients, such as many fragrances and flavours, where loss through evaporation needs to be prevented. Furthermore, the smaller the particles, comprising potentially combustible active ingredients, the higher the risks of explosion while handling, thus requiring particular handling precautions which have a bearing on cost-efficiency.

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Spray-drying methods, for example, have been used for some time to encapsulate flavours and/or fragrances in glassy matrices and are extensively disclosed in the prior art. Typically, drops of a suspension are sprayed through a nozzle in a spraying tower where they are exposed to hot air, causing the evaporation of water and thus formation of dried particles which are generally collected at the bottom of the drying tower. However, typical spray-drying is not suitable to produce capsules of higher than about 100 µm, because drying of these large drops would not be sufficiently quick to prevent sticking of the drops to the inner wall of the tower. A further drawback of traditional spray-drying methods is the fact that relatively low viscosity suspensions or emulsions have to be employed, with a viscosity upper limit of about a few hundred mPas, in order to allow reliable atomisation. Low viscosity is generally achieved with a high water content (about 40 wt.%) of the reactive mixture, but this in turn requires evaporation of the water during the drying process. It goes without saying that a drying process in which high amounts of water need to be removed is more costly. From the above it can clearly be deduced that spray-drying is not suitable for producing particles having a particle size in the range of 100 – 2000 µm. In addition, while being rather simple and well understood, spray-drying only allows processing of low viscosity slurries.

The prior art of pertinence in the field of the invention has addressed the shortcomings of traditional spray-drying methods. For example, WO 04/062382 describes a process for producing beadlet preparations of fat-soluble substances, wherein an aqueous suspension of a fat-soluble substance is fed into a spray tower while simultaneously introducing powder starch and hot air, through separate inlets, into the spraying tower. This process is said to be carried out at a temperature of up to 200°C, but preferably from 60-120°C in the spray zone, and the fat-soluble substance is a vitamin, such as vitamins A, D, E, K, a carotenoid, a polyunsaturated fatty acid, an oil or a fat. The latter are substances which are not particularly volatile and could therefore be optimally preserved in relatively dense beadlets. There is no mention however of the problems that may be encountered when trying to encapsulate volatile substances, which require particular precautions against evaporation, nor of the encapsulation of hydrophilic actives, not soluble in fats and which constitute a particular interest of the present invention.

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WO 91/17821 describes a process for preparing microcapsules containing a flavorant embedded in a matrix material by spraying an aqueous suspension under the supply of air having a temperature of 50 to 120°C, while simultaneously introducing a spraying agent. The spraying agent may comprise starch, modified starch, tri-calcium phosphate and others. This reference clearly states that in conventional spray drying hot air having a temperature of typically 180-300°C is supplied. Furthermore, several disadvantages of spray-drying are mentioned, and it is indicated that bigger particles than those obtained by spray drying would be desirable and provide advantages.

Moreover, from some examples of WO 91/17821 it can be seen that the encapsulation process according to this teaching suffers a substantial loss of up to 50 wt.% of the flavourant material present in the initial emulsion (Examples 1, 3 and 4).

The aim of the present invention is precisely to produce flavour and/or fragrance particles in a way that reduces substantially the flavor losses, for example, that not more than 20 wt.%, and preferably less than 10 wt.% of the flavour and/or fragrance material is lost during the preparation of the capsules. It is a further objective to obtain capsules with a higher flavour/fragrance load.

Summary of the Invention

According to the invention there is provided a process for encapsulating volatile ingredients in capsules having a diameter in the range of 100 to 2000 µm, and more preferably between 200 and 800 µm, wherein the ingredient to be encapsulated is sprayed into a cloud of powdering agent, the process being characterized in that the temperature of the air supplied into the tower for drying is above 121°C. Surprisingly, the loss of volatiles remained significantly lower than in processes of the prior art, where lower temperatures of the supplied air are used.

Accordingly, the present invention provides, in a first aspect, a method for preparing capsules having an average diameter in the range of 100 to 2000 µm encapsulating a flavour and/or fragrance ingredient (hereinafter "ingredient"), the method comprising the steps of

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- a) preparing an aqueous solution, suspension and/or emulsion (hereinafter simply "emulsion") comprising the flavour and/or fragrance ingredient in a dissolved, suspended and/or emulsified form (hereinafter simply "emulsified"), matrix materials and water,
- b) spraying the emulsion in the form of drops having a mean diameter of 100 to 2000 μm into a spraying tower,
- c) introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower to obtain a coating of powdering agent on the drops of the sprayed emulsion,
- d) supplying, simultaneously to the spraying step, a hot gas into the spraying tower, and,
- e) removing capsules comprising a coating of powdering agent from the spraying tower,

the process being characterized in that the temperature of the hot gas supplied in step e) is in the range of 130 – 250°C.

The present invention also relates to the capsules obtainable by the method of the invention, which present a content in encapsulated material which is surprisingly high compared to those that could be obtained with prior art processes of the same type.

Thus, the present invention further provides capsules having an average diameter in the range of 100 to 2000 μm encapsulating a flavour and/or fragrance ingredient, the load of the ingredient being in the range of 18-50 wt.%, preferably 20-40 wt.%, the capsules being provided with a powdering agent coating, whereby the coating provides 0.1 to 30 wt% of the total weight of the capsule.

In a fourth aspect, the present invention provides a method for reducing loss of flavour and/or fragrance ingredient during the preparation of capsules having an average diameter in the range of 100 to 2000 μm, the method comprising the step of dispersing a suspension and/or emulsion comprising the flavour and/or fragrance ingredient, matrix materials and water into a spraying tower, wherein the spraying tower is further supplied with a hot gas having a temperature in the range of 130 to 250°C and wherein simultaneously a powdering agent is introduced into the spraying tower.

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In a fifth aspect, the present invention provides the use of a multi stage drying apparatus for preparing capsules according to the method of the present invention.

The process of the present invention provides a number of important advantages over the processes known from the prior art. First of all, the fact that higher temperatures may be used leads to a substantial reduction of loss of ingredient. The higher temperature also enables shorter residence time of the capsules in the tower and/or fluidised bed, which allows for a more speedy process. The higher temperatures allow quicker drying and, as a consequence, less drying/powdering agent needs to be added than in the prior art methods. Accordingly, the coating provided by the powdering agent is substantially thinner. This, in turn, allows for higher load of the active ingredient in the capsules

Brief Description of the Drawing

Figure 1 shows the loss of limonene during encapsulation in a glassy matrix in a multi-stage drying apparatus at air inlet temperatures according to the present invention. It can be seen that by spraying drops of an emulsion comprising limonene into a circulating suspension of native starch in the drying tower, higher temperature of the main inlet air stream results in lower loss of flavour, with better results being obtained at 170°C than at 140°C.

Description of the Detailed Embodiments of the Invention

The present invention provides a method for preparing capsules having an average diameter in the range of 100 to 2000 µm encapsulating a flavour and/ or fragrance ingredient. Preferably, the average diameter is in the range of 200 to 800 µm, more preferably 300 to 500 µm. The term "average" and/or "mean" as used, for example, in the expression "average diameter", refers to the arithmetic mean.

The method of the present invention may be performed in any conventional spraying tower such as described in WO 2004/062382 (page 2, lines 26-35), for example.
Surprisingly, it has now been established that a conventional multi-stage drying apparatus can be used for conducting the steps of the method of the present invention. A multi-stage

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drying apparatus comprises a spray drying tower, and, at the bottom of the tower, a fluidised bed intercepting partially dried particles which have fallen across the tower. In a typical multi-stage drier, an air inlet and an air outlet are situated in the upper region of the tower. Generally, it is possible to maintain, in these devices, a suspension of fine particles herein referred to as a "powdering agent", as is required for the purpose of the present invention. The powdering agent is generally introduced by a separate inlet that may preferably be situated either close to the inlet of the aqueous emulsion or in the lower part of the drying tower. The powdering agent is, in the operation mode, in constant movement and may exit the tower together with the air outlet.

The present invention thus provides a new utility of classic multi stage spray driers and, in addition enables the preparation of relatively large-sized capsules according to the method herein disclosed with a non-specialised equipment. The use of such a multistage dryer enlarges the encapsulation possibilities and variety. Accordingly, in an embodiment, the invention provides a method which is conducted in a multi stage drying apparatus.

The capsules produced according to the present invention have an average diameter in the range of 100 to 2000 μm. The size of the capsules is determined by the size of the drops that are dispersed into the drying tower according to a step of the method of the invention. According to an embodiment of the invention, the step of dispersing the emulsion is performed by guiding the emulsion through a spraying nozzle or through a centrifugal wheel disk into the spraying tower. Other devices may be used to disperse the emulsion in the form of drops of a controlled average size. For instance vibrated orifices may be used instead.

If a spraying nozzle is used for dispersing the drops the size may be controlled by the flow rate of an atomising gas through the nozzle, for example.

In the case where a centrifugal wheel disk is used for dispersal, the main factor for adjusting droplet size to the terms of the present invention is the centrifugal force with which the drops are dispersed from the disk into the tower. The centrifugal force, in turn, depends on the speed of rotation and the diameter of the disk. The feed flow rate of the emulsion, its viscosity and surface tension are also parameters controlling the final drop size and size distribution. By adjusting these parameters, the skilled person can control the size of the drops of the emulsion to be dispersed in the tower.

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The method of the present invention comprises the step of preparing an aqueous solution, suspension and/or emulsion (hereinafter simply "emulsion") comprising the flavour and/or fragrance ingredient in a dissolved, suspended and/or emulsified form, matrix materials and water.

Within the context of this specification the word "comprises" is taken to mean "includes, among other things". It is not intended to be construed as "consists only of".

The flavour and/or fragrance ingredient may thus be mixed with a carrier system by dissolving it together with a matrix material, by suspending and/or by emulsifying it therein. For the sake of convenience, the term emulsifying is used to encompass all the different forms of mixing the ingredient with the inert matrix materials.

The ingredient may be hydrophilic and/or hydrophobic. Accordingly, the invention is applicable to a large family of ingredients including water soluble ones, such as juices, reaction flavours, for example. The ingredient may also comprise a combination of hydrophilic and hydrophobic components. If the ingredient is hydrophilic, it will generally be dissolved in the aqueous solution together with the matrix materials. According to a preferred embodiment, the ingredient comprises hydrophobic components, while the matrix materials may be soluble in water. Generally, in this case, the hydrophobic ingredient is emulsified in the form of small droplets having an average diameter in the range of 0.5-10 μm, preferably 1-5 μm for example, within the matrix materials. Emulsification may be made, for example, by using a high pressure homogeniser or a colloid mill.

A flavour and/or or fragrance ingredient, herein referred to as "ingredient" encompasses flavour and fragrance ingredients or compositions of current use in the flavour and/or fragrance industry, of both natural and synthetic origin. It includes single compounds and mixtures. The capsules used in the invention can encapsulate volatile or labile ingredients in liquid form, preferably with a log P in the range of -2 and 7, preferably 2 - 6. Specific examples of such components may be found in the current literature, e.g. in Fenaroli's Handbook of flavour ingredients, 1975, CRC Press; Synthetic Food adjuncts, 1947 by

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M.B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander, 1969, Montclair, New Jersey (USA). Many other examples of current perfumery ingredients to be encapsulated as herein taught may be found in the patent and general literature available.

Accordingly, in a preferred embodiment, the ingredient is selected from the group consisting of a flavour and/or fragrance compound or composition, a flavour or fragrance natural extract, and a mixture of any of the before mentioned ingredients.

Flavour and/or fragrance ingredients are well known to a person skilled in the art of aromatising and/or providing a pleasant odour to consumer products, i.e. of imparting an odour or a flavour or taste to a consumer product, or of modifying the taste and/or odour of said consumer product, or yet its texture or mouthfeel. Natural extracts can also be encapsulated into the system for flavouring or perfuming consumer end products. Examples of these include citrus extracts such as lemon, orange, lime, grapefruit, or mandarin oils or coffee, tea, mint, cocoa or essential oils of herbs and spices between other.

Other examples of flavour and/or fragrance ingredients are synthetic flavour and/or fragrance oils, flavouring aromatics and natural extracts such as oils, essential oils, oleoresins and other extracts derived from plants, for example from leaves, flowers, fruits, roots, rhizomes, stem, and so forth.

Other flavours included by the term ingredient are reaction flavours, or process flavours. These flavours may be obtained by heating food ingredients and/or ingredients, which are permitted for use in foodstuffs or in process flavourings. A nitrogen source and a carbohydrate source are necessary to perform a Maillard reaction for obtaining process flavours.

The flavour and/or fragrance ingredient may be present in the form of a mixture with solvents, adjuvants, additives and/or other components, generally those of current use in the fragrance and/or flavour industry.

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Preferably, the ingredient or composition is liquid at 60°C. More preferably, it is liquid at 40°C. Most preferably, it is liquid at room temperature (RT= 25°C).

A typical characteristic of flavour and/or fragrance compositions is the high proportion of volatile compounds and/or components. Accordingly, in an embodiment, the active ingredient or composition to be encapsulated according to the invention comprises at least 10 wt.%, preferably at least 20 wt.%, more preferably at least 30 wt.% and most preferably at least 40 wt.% by weight, relative to the weight of the composition, of chemical compounds having a vapour pressure of ≥ 0.007 Pa at 25°C.

Preferably, at least 10 wt.% by weight have a vapour pressure of ≥ 0.1, more preferably at least 10 wt.% have a vapour pressure of ≥ 1 Pa at 25°C, and most preferably, at least 10 wt.% have a vapour pressure of ≥ 10 Pa at 25°C.
Compounds having a vapour pressure equal to or above 0.007 Pa at 25°C are generally regarded as having a volatile character and benefit the most from encapsulation processing.
The limit of 10 wt.% of such compounds is regarded to constitute a substantial part of the active ingredient or composition. The method of the present invention, however, also allows for efficient encapsulation of more volatile ingredients, present in higher amounts in the composition than those cited above.

For the purpose of the present invention and for the sake of convenience, the vapour pressure is determined by calculation. Accordingly, the method disclosed in "EPI suite"; 2000 U.S. Environmental Protection Agency, is used herein to determine and define the concrete value of the vapour pressure of a specific compound or component of the active ingredient. This software is freely available and is based on average values of vapour pressures obtained by various scientific methods.

In the context of the present invention, percentages relative to the capsules are percentages by weight of dry matter, unless otherwise indicated. Similarly, if proportions are indicated as parts, parts of weight of dry matter are meant. In case that water is indicated as part of a composition, such as a composition of different ingredients, of a

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solution, emulsion, for example, percentages refer, of course, to the total weight of the composition, including water.

Matrix materials useful in the preparation of an emulsion in a step of the present invention have the purpose of providing a carrier for the ingredient. Preferably, the matrix materials are selected as to their capacity of forming a glassy matrix during the drying of the emulsified dispersed drops. A glassy matrix is an amorphous solid characterized by viscosities of the order in the range of about 10^{10} to 10^{12} Pa*s and an extremely low molecular mobility. A good understanding of the glassy state is provided by Dominique Champion *et al* in "Towards an improved understanding of glass transition and relaxations in foods: molecular mobility in the glass transition range", Trends in Food Science and Technology 11 (2000) 41-55.

Matrix components may be selected, for example, from polymers, namely proteins, polymeric carbohydrates, and other polymeric materials. The polymeric materials preferably comprise hydrophilic polymers in order to provide an effective oxygen-barrier. Accordingly, the matrix may comprise hydrocolloids. In addition, polymers being less soluble in water, that is, more hydrophobic polymers may be present in the matrix, too, in order to provide some lipophilic character to the glassy matrix and thus to provide protection against moisture. In addition, the matrix may contain further components that are not polymeric, buts that may assist in the formation of a dense glassy matrix or that may be added for another purpose.

Suitable matrix components optionally associated with or part of the flavour capsules of the invention may thus comprise proteins, for example caseins, whey proteins, soy protein, and/or gelatine, for example. These proteins have good emulsification and film forming properties and can thus form the basis for polymer matrices. Preferably, the matrix components comprise carbohydrates. The matrix components may comprise water soluble and non-water soluble carbohydrates.

For example the matrix component may comprise monosaccharides, disaccharides, trisaccharides and/or oligosaccharides, for example. Accordingly, in a preferred

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embodiment of the present invention, the matrix materials comprise polysaccharides, and, in addition, saccharides selected from the group of mono- and/or disaccharides.

Preferably, the matrix component comprises polysaccharides, that is, saccharides containing more than 10 monosaccharide units per molecule. Likewise, the matrix component may comprise gums and/or hydrocolloids, for example, gum arabic and the like.

More preferably, the matrix component comprises a starch and/or a starch derivative such as pre-gelatinised starch, thin- or thick- boiling starch, dextrins or maltodextrins of various molecular weights. Other possible modifications of starch and resulting derivatives suitable as a matrix component include octenyl-succinated starch, starch ethers (i.e. carboxymethyl starch), starch esters (i.e starch monophosphate), crosslinked starch and/or oxidised starch.

Preferably, the matrix component comprises dextrin, more preferably maltodextrin and/or corn syrup. Most preferably, the matrix component comprises maltodextrin and/or corn starch syrup having a mean dextrose equivalence of 5-25, preferably 6-20, more preferably 10-18.

In a preferred embodiment, the matrix component comprises, per dry weight of the glassy matrix alone, 60-95 wt.% of maltodextrin, preferably with a DE value in the above indicated ranges, and 5-40 wt.% of modified starch, such as alkenyl-succinated starch, (in particular octenyl-succinated starch).

While the above matrix-materials are preferred in case of applications of the capsules to food products and/or beverages, there may be numerous further materials suitable in case that the capsules are not intended for addition to food products. For example, in capsules comprising fragrance ingredients, the matrix material may be selected from a much wider range of materials. For example, synthetic polymers, co-polymers or natural non-food polymers, salts and other fillers may be used as matrix materials.

The emulsion prepared in a step of the present method preferably comprises 10-70 wt.% of matrix materials, 30-70 wt.% of water and 5-35 wt.% of the active ingredient or

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composition to be encapsulated. More preferably, the percentages are respectively in the ranges of 20-40, 40-60 and 10-30 wt.%, and most preferably in the ranges 25-35, 45-55 and 15-20 wt.% of matrix materials, water and ingredient, respectively, in the emulsion.

According to a preferred embodiment of the method of present invention, the emulsion comprising the ingredient, matrix components and water has a dry matter content in the range of 45-80 wt.%, preferably 50-70 wt.%. The relatively high dry-matter content provides a high viscosity emulsion, the latter possibly presenting difficulties in handling and guidance into the spraying tower. On the other hand, thanks to a high dry-matter content, the drying process becomes more efficient as less water needs to be evaporated. Unlike in conventional spray drying, where the emulsion viscosity needs to be low enough to produce fine droplets having a diameter of generally less than 150 µm, the present invention enables the preparation of comparatively large drops to be dried successfully and efficiently. In this case, it is not necessary for the emulsion to have a low viscosity, but, if compared to conventional spray drying, higher viscosities may be used.

Such emulsions with high dry-matter content lead to the large size capsules of the present invention, resulting from the large size drops dispersed in the drying tower.

The present invention comprises a step of introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower to obtain a coating of powdering agent on the drops of the sprayed emulsion. According to a preferred embodiment, the powdering agent is selected from the group consisting of starch, starch derivatives, talc, bentonite, silicon dioxide, calcium, magnesium, aluminium or potassium silicates, sodium, potassium or calcium aluminosilicates, calcium, sodium, or magnesium carbonates, calcium or magnesium phosphates, ferric ammonium citrate, microcrystalline cellulose and cellulose derivatives or fibers, aluminium, calcium, sodium, magnesium, potassium or ammonium salts of fatty acids, magnesium oxides and mixtures comprising two or more of the aforementioned powdering agents. The purpose of the powdering agent is to prevent the dispersed drops from attaching to each other and/or to the inner walls of the spraying tower. The powdering agent is thus suspended in the tower and creates a coating on the dispersed drops as soon as they enter the tower. Accordingly, in a preferred embodiment of the invention, particles of the powdering agent are suspended in the

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spraying tower and circulate from an inlet to an outlet of the spraying tower, which outlet is also the outlet of the hot gas.

Generally, the powdering agent itself is circulating from the inlet into the drying tower, from which it generally exits together with exhaust gas at the exhaust gas outlet. The powdering agent may be recycled in a cyclone collector from which it may be redirected by a powdering agent return pipe to the inlet into the spraying tower. Preferably, the powdering circulates at least in part in counter current with the dispersed drops. Accordingly, in a preferred embodiment of the invention, spare powdering agent not absorbed on the dispersed capsules exits the spraying tower together with the hot gas through an outlet of exhaust gas, which leads to a cyclone or a filter bag house able to separate the hot gas from the powdering agent, the powdering agent being then re-introduced into the spraying tower. There is thus a continuous circulation of powdering agent from the cyclone to the spraying tower and back to the cyclone.

The method of the present invention comprises the essential step of supplying, simultaneously to the dispersing step, a hot gas having a temperature in the range of 130-250°C into the spraying tower. The hot gas is supplied at a higher temperature than that disclosed in the prior art, in particular in WO 91/17821, and also higher than the preferred temperature of WO 04/062382, the latter not relating to the encapsulation of flavours and/or fragrance ingredients, that is, generally volatile ingredients.
It was surprisingly established that relatively large-sized drops comprising the encapsulated ingredient are preferably dried under supply of a gas having a higher temperature than that prior taught, whilst simultaneously improving on the loss of volatiles during drying.

This result is totally unexpected, as it is well-known in the art of spray drying encapsulation methods that the use higher drying temperatures generally entails a higher loss of volatiles. Without wishing to be bound by theory, it is hypothesized that the higher temperature in the spraying zone brought about by the higher temperature of the inlet gas stream results in a shorter drying time. According to the invention, more water is evaporated from the droplet during its flight at high temperature, and the subsequent drying time in the fluidised bed can thus be shortened.. It is believed that the subsequent

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drying by hot air in the fluidised bed takes longer in the prior art methods and may result in substantial further loss or degradation of ingredients.

According to a preferred embodiment, the hot gas supplied into the drying tower has a temperature in the range of 135–220°C, preferably 140-210°C, and most preferably 150-190°C.

The hot gas may be air or nitrogen, for example.

The supply of hot gas through a hot gas inlet results in a temperature in the spraying tower in the range of about 180 to about 50°C, preferably about 170°C to about 40°C. The temperature in the tower follows a gradient, with the highest temperature at the hot gas inlet, which thus provides a high temperature at the spraying zone. At the bottom of the tower the temperature is much lower, due to the evaporation of water from the dispersed drops.

The method of the invention also comprises the step of removing the capsules coated with powdering agent from the spraying tower.

The method of the present invention described above may be carried out batch-wise or continuously. In a multi-stage drier, a batch-wise operation may be chosen. Accordingly, there is an exit at the level of the fluidised bed leading to a collecting vessel. By switching off the fluidised bed and opening the valve leading to the collecting vessel, capsules are guided, for example by gravity, to the collecting vessel, from where they may be removed. In a preferred embodiment, the method of the invention is performed continuously, for example by conveying the granules from the integrated fluidised bed to an external, additional fluidised bed where the capsules may be further dried to accurately control their final moisture content. In practice, according to the process of the invention, the residence time of the capsules in the whole process is reduced, resulting in a better quality product.

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According to a preferred embodiment, the method of the invention comprises a further step of intercepting the capsules by a fluidised bed after being coated by the powdering agent and after being at least superficially dried by the hot gas in the spraying tower.

Preferably, the fluidised bed is supplied with a gas having a temperature in the range of 40 to about 100°C, meaning that gas having a temperature in this range is supplied from below the bed through small apertures to fluidise / intercept the capsules. Preferably, the temperature of the gas is in the range of 65 to 90°C. Generally, the gas is air. Similarly to the spraying zone, the method of the present invention again provides for comparatively high temperatures in the fluidised bed in view of the prior art. Again a shorter drying period has resulted in surprisingly lower loss of volatile ingredients.

The capsules obtainable and/or obtained by the method of the present invention will have a flavour and/or fragrance ingredient load of 1–50 wt.%. According to a preferred embodiment, the load of the ingredient is in the range of 18–50 wt.%. It is thus possible to have high ingredient loads in the range of 20–40 wt.%, preferably 25–38 wt.% and more preferably 27 to 35 wt.%. The high ingredient loads obtainable by the present invention are a result of the use of comparatively high temperatures of the inlet gas and are clearly superior to volatile ingredient loads obtained by similar processes of the prior art. The high loads are further a consequence of reduced loss of volatiles achieved by the present method.

The high ingredient loads of the capsules of the invention are thus also a consequence of the comparatively low relative contribution of the coating provided by the powdering agent on the surface of the capsules of the invention. Of course, the term "surface" in this context does not exclude the possibility of one or more further outer coatings, possibly coating the layer provided by the powdering agent. For example, one can easily envisage a further lipid-based coating.

Generally, the contribution of the powdering agent to the total weight of the capsules may be in the range of 0.1 to 30% by weight, which corresponds to a preferred embodiment of capsules according to the present invention. However, the amount of powdering agent may be lower, from 0.1 to 27 wt.%, preferably from 0.5 to 25 wt.%, more preferably from

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1 to 20 wt.% and most preferably from 12 to 15 wt.% of powdering agent. In most advantageous embodiment, the amount of powdering agent makes up ≤ 10 wt.% of the total weight of the capsules of the present invention.

The present invention further provides capsules obtainable and/or obtained by the method of the present invention.

The present invention provides a food product comprising the capsules of the invention and/or the capsules obtainable by the method of the invention. Products may be, for example, food products, in which the encapsulated ingredient is a flavouring ingredient.

The present invention further encompassed perfumed products comprising the capsules of the invention, in which the ingredient is a perfuming composition, for example a perfume, an eau-de-toilette, or another composition of perfuming ingredients, optionally further comprising solvents and/or other adjuvants. Preferred consumer products thus perfumed include solid detergents, soaps and cleaners in particular.

The following examples illustrate the practice of this invention and its preferred modes. It will be understood, however, that these examples are not intended to limit the scope of the invention. Other embodiments of the capsules of the present invention may readily be prepared on the basis of the general teaching herein and the following examples.

Examples

Examples 1-8 below were carried out with samples prepared on the basis of the components listed in Table 1. In addition, the table indicates the results obtained in each case, such as the content of the final starch fraction, final flavour load and flavour loss during the preparation process. In all examples, vapour pressure is expressed in Pa at 25°C and was determined for each ingredient compound with the "EPI suite" software mentioned above.The results of examples 1 to 8 are also summarized in Figure 1.

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Example 1

Drying of formula 1 with inlet air at 140°C

A solution was prepared by mixing 295 g of Capsul® (supplied by National Strarch), 5 g of citric acid and 500 g of warm water at 50°C in a vessel until the starch was completely dissolved. The solution was then maintained at 40°C under gentle stirring. 200 G of limonene were poured into the above-described solution, and homogenized using a high shear rotor/stator mixer Ultra Turrax T50 rotating at 10000 rpm, until the average droplet size of the emulsion was below 2 microns. Limonene has a vapour pressure of 193 Pa.

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Table 1: Inlet temperatures and compositions of matrix materials with respective flavour loss

For-mula	Example	PG (g)	Sucrose (g)	Capsul® (g)	Citr. ac. (g)	Limonene (g)	H_2O (g)	Inlet gas T°C	Final native starch (coating) fraction w/w	Final flavour load w/w	Flavour loss %
1	1	-	-	295	5	200	500	140	12.1	32.0	14.1
	2	-	-	295	5	200	500	170	10.4	34.7	5.2
2	3	-	50	245	5	200	500	140	10.6	30.9	20.8
	4	-	50	245	5	200	500	170	10.0	32.3	16.0
3	5	50	50	195	5	200	500	140	18.3	25.0	33.9
	6	50	50	195	5	200	500	170	17.8	27.2	25.8
4	7	50	-	245	5	200	500	140	21.8	23.2	36.7
	8	50	-	245	5	200	500	170	14.3	30.5	17.1

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200 G of native Starch type B from Roquette Frères SA were first introduced into a pilot plant multi-stage drier (Niro FSD0.8) and recycled in closed loop continuously all along the process since this dryer is equipped to return the fine particles back into the drying chamber. A cloud of native starch particles was thus created inside the drier.

After 10 minutes, the emulsion was sprayed into this cloud using a two-fluid nozzle. This nozzle had a diameter of 1 mm and was fed with compressed air at a rate of 25 ml/min. The feed flow rate was maintained at 0.057 l/min using a gear pump.

The main air stream arriving on top of the chamber was maintained at 140°C with a flow rate of 60 kg/h. The fluid bed fitted at the bottom of the chamber was fed at a rate of 22 kg/h with warm air at 50°C.

The third air stream conveying the powdery agent back into the chamber was heated at 50°C and its flow rate was 10 kg/h.

Since a fix feed flow rate was used, the outlet air temperature of the dryer depended on the amount of water evaporated in the dryer, as well as on the nature (hygroscopicity) of the encapsulating matrix.

The feed was sprayed during 10 minutes and the atomization was then stopped. The granules collected in the fluidized bed were kept in fluidization during 15 more minutes to finish the drying and control their final residual moisture content.

180 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. After discarding the granules having a size below 100 microns and above 700 microns their average diameter was of 350 microns.

Dissolving a fixed amount of granules in cold water and filtering the product, the native starch particles were collected and, after drying, the final amount of dry native starch present in the granules was evaluated. This value was used to calculate the flavor loss.

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In this example, 3.5% w/w of native starch was present in the final granules and since the final flavor load was 34% w/w, the flavor loss was 18% w/w of the initial amount of flavor used.

Example 2

Drying of formula 1 with inlet air at 170°C

The same formulation and preparing conditions were used as in Example 1.

The processing conditions were all the same except that the main air stream was heated at 170°C.

In this example, 10.1% w/w of native starch was present in the final granules. The final flavor load was 34.7% w/w and the limonene loss was only 5.2% w/w of the initial amount.

Examples 3 and 4

Drying of formula 2 with inlet air at 140°C and 170°C respectively.

A formulation using some sucrose in the encapsulating matrix was prepared (see Table 1). The same preparing conditions were used as in Example 1.

The processing conditions were all the same as in Example 1. The inlet air temperature was 140°C and 170°C in Example 3 and 4, respectively.

In Example 3, 10.6% w/w of native starch was present in the final granules. The final flavor load was 30.9% w/w and the limonene loss was 20.8% w/w of the initial amount, which is rather economically significant.

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In Example 4, where the granules were dried at higher inlet air temperature, 10.0% w/w of native starch was present in the final granules. The final flavor load was 32.3% w/w and the limonene loss was then only 16.0% w/w of the initial amount.

Examples 5 and 6

Drying of formula 3 with inlet air at 140°C and 170°C respectively.

A formulation using some sucrose and propylene glycol in (PG) in the encapsulating matrix was prepared (see Table 1). The same preparing conditions were used as in Example 1. Sucrose and propylene glycol were dissolved together with Capsul® and citric acid

The processing conditions were all the same as in Example 1. The inlet air temperature was 140°C and 170°C in Example 5 and 6, respectively.

In Example 5, 18.3% w/w of native starch was present in the final granules. The final flavor load was 25.0% w/w and the limonene loss was 33.9% w/w of the initial amount.

In example 6 the granules were dried at higher inlet air temperature, and 17.8% w/w of native starch was present in the final granules. The final flavor load was 27.2% w/w and the limonene loss was then 25.8% w/w of the initial amount.

Examples 7 and 8

Drying of formula 4 with inlet air at 140°C and 170°C respectively

A formulation using some propylene glycol and no sucrose in the encapsulating matrix was prepared (see Table 1). The same preparing conditions were used as in Example 1. Propylene glycol was dissolved together with Capsul® and citric acid

The processing conditions were all the same as in Example 1. The inlet air temperature was 140°C and 170°C in Example 7 and 8 respectively.

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In Example 7, 21.8% w/w of native starch was present in the final granules. The final flavor load was only 23.2% w/w and the limonene loss was 36.7% w/w of the initial amount.

In Example 8 the granules were dried at higher inlet air temperature, and 14.3% w/w of native starch was present in the final granules. The final flavor load was 30.5% w/w and the limonene loss was much smaller than in Example 7 with only 17.1% w/w of the initial amount of limonene being lost.

Example 9

Encapsulated Strawberry Flavour

A solution was prepared by mixing 300 g of Capsul®, 250 g of Maltodextrine 18DE and 50 g sucrose in 754 g of warm water at 50°C until complete dissolution of the ingredients. The solution was then maintained at 40°C under gentle stirring. 400 G of a strawberry type flavor (origin: Firmenich SA, Geneva, Switzerland) was poured into the above describe solution, and homogenized using a high shear rotor/stator mixer Ultra Turrax T50 rotating at 10000 rpm.

The strawberry flavour comprised 83 wt.% of solvant (triacetine, the vapour pressure (vp) of which is 0.698 Pa). 17 wt.% of the strawberry flavour is thus provided by flavour ingredients, of which Furaneol® (tradename of Firmenich SA; 14.7 wt.% of ingredients, vp = 0.125 Pa) and ethyl butyrate (14.7 wt.% of ingredients, vp = 1964 Pa) are the most significant constituents. Further ingredients of the strawberry flavour were 2-methyl butanoic acid (5.9 wt.% of ingredients, vp = 149 Pa) and ethyl-2-methyl butanoate (5.9 wt.% of ingredients, vp = 1070 Pa), amongst others.

The same process as in Example 1 was used, except for the main air stream inlet temperature that was 190°C and the fluid bed gas temperature that was 75°C. After discarding the capsules having a size below 200 microns and above 500 microns their average diameter was of 350 microns. In this example, 5.8 wt.% of native starch

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(powdering agent) was present in the final capsules (coating). The final flavour load was 35.2 wt.% and thus the flavour loss was 10% w/w of the initial amount of flavour used.

Example 10

Encapsulated Mint Flavour

A solution was prepared by mixing 300 g of Capsul®, 250 g of Maltodextrine 18DE and 50 g sucrose in 754 g of warm water at 50°C until complete dissolution of the ingredients. The solution was then maintained at 40°C under gentle stirring. The menthol was dissolved in a mint flavour and 400 g of this flavour mixture was poured into the above described solution, and homogenized using a high shear rotor/stator mixer Ultra Turrax T50 rotating at 10000 rpm. More than 10 wt.% of the flavour ingredients of the mint flavour were provided by compounds having a vapour pressure above 1 Pa.

The same process was used as in Example 9. After discarding the capsules having a size below 200 microns and above 500 microns their average diameter was of 350 microns. The capsules obtained had 7.1 wt.% of native starch (coating) and a final flavour load of 33.3 wt.%.

Examples 11 and 12

Food Products Comprising the Capsules of the Invention

Example 11

Sugar-free Chewing Gum Comprising Encapsulated Flavours

Sugar-free chewing gum was prepared with the ingredients given below:

Ingredients	Percent (%)
Gum base (Cafosa® Gum Base Co., Spain)	30.00
Crystalline sorbitol powder	53.85
Mannitol powder	4.00

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Sorbitol 70% solution	10.00
Glycerine	2.00
Acesulfame potassium	0.05
Aspartame®	0.10
Total	100.00

Chewing gums were prepared according to the following, general procedure: crystalline sorbitol, mannitol, acesulfame potassium and Aspartame® were dry blended forming a powder of blended sweeteners. Half of the sweetener's blend was added to a sigma-blade mixer. The gum base was heated to soften it and added to the sigma blade mixer (equipped with a heated water jacket to allow mixing at a temperature of about 55°C) and mixed for 2 min. Thereafter, the remaining sweetener's blend and all liquid ingredients (sorbitol 70% solution and glycerine) were added to the mixer and further mixed for 7 min. After a total mixing time of 12 minutes, the unflavoured gum base was removed and encapsulated flavours were added thereto (see below). The flavoured gum base was then shaped into the desired thickness and passed through a pellets forming machine (LWS80 from Hermann Linden, Maschinenfabrik GmbH & Co KG, Germany) to make small chewing gum pellets of 2 g each.

Four different samples of chewing gums were thus prepared based on iso-loads of strawberry and mint flavours, respectively. One of these samples was flavoured with 0.57 wt.% of the capsules of Example 9, and, for comparison, one sample was flavoured by addition of an iso-load of strawberry flavour encapsulated by conventional spray drying.

In samples 3 and 4, similarly, chewing gums were flavoured with mint flavour by adding 0.6 wt.% of the capsules of Example 10, and, for comparison, by adding an iso-load of mint flavour encapsulated by conventional spray drying.

In sensory evaluation blind tests, trained panellists found a higher sensory boosting impact and a higher perceived flavour intensity, when chewing the mint-flavoured chewing gum comprising the capsules of the invention, as compared to the analogue flavoured with conventionally spray dried capsules.

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Example 12

Sugar-free Hard-Boiled Candy Comprising Encapsulated Flavours

Sugar-free hard-boiled candies were prepared with the ingredients given below:

Ingredients	Percent (%)
Part 1	
Aspartame®	10.00
Acesulfame potassium	5.00
Water	85.00
Total	100.00
Part 2	
Citric acid solution (50% solids)	0.75
Part 3	
Isomalt®	100.00
Water	30.00
Total	100.00

Aspartame® and acesulfame potassium were dry blended forming a powder, slowly added into water and mixed to form a homogeneous high intensity sweetener solution.

In a copper pan, 100 g of Isomalt® and 30 g of water were added. The contents of the copper pan were heated to 160°C under stirring in a gas cooker. At 160°C, the copper pan was removed from the cooker and placed in a water bath at 40°C, and then removed after a few seconds.

For strawberry flavour: When the temperature had reached 135°C, the high intensity sweetener solution (1.0 ml) was added to the Isomalt mixture, followed by addition of the

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citric acid solution (1.50 ml) and mixed with a spatula. 0.17 wt.% of flavour capsules (Example 9) were carefully added by spreading them on the top surface of molten candy and mixing them well into the molten candy, resulting in 100 wt.% of molten candy including the encapsulated flavour. Finally, the molten candy was poured into ejector-pins of the Teflon® mould. After solidification, the sugar-free hard-boiled candies were manually ejected from the ejector-pins of the Teflon® mould.

For Mint flavour: When the temperature had reached 135°C, the high intensity sweetener solution (1.0 ml) was added and mixed with a spatula. 0.81 wt.% of encapsulated flavor capsules (Example 10) were carefully added by spreading them on the top surface of molten candy and mixing them well into the molten candy, resulting in 100 wt.% of molten candy including the encapsulated flavour. Finally, the molten candy was poured to solidify as described above.

The hard-boiled candies of the invention were compared on blind tests by sensory panel individuals against hard-boiled candies containing iso-loads of strawberry and mint flavours, respectively, encapsulated, however, by screw-extruding molten carrier mass comprising flavours emulsified therein. The hard-boiled candies containing the capsules of the invention had the same initial boosting impact, but exhibited higher flavour intensity over time than the hard-boiled candies flavoured with the capsules obtained by conventional screw-extrusion.

Examples 13 to 16

Food Products Comprising the Capsules of the Invention

The in-dough performance of the flavored capsules of the invention was compared with liquid and conventionally spray dried formats for different flavor tonalities. The tonalities that were evaluated in cookie and cracker food products are shown in Table II. The *American Association of Cereal Chemists* method (*AACC*)-10-50D was used to prepare cookies.

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Table II: Flavor Tonalities evaluated in different applications

Food Application	Flavor Tonality
Cookies	Butter
Chocolate Cookies	Mint
Crackers	Butter
Cheese Crackers	Bacon

The cookies and crackers were prepared in conventional manner using the formulae indicated herebelow, to which there were added iso amounts of each of the appropriate flavors indicated in table II, in three forms for comparison: flavor in liquid form, as a conventional spray dried powder and as powder capsule form obtained according to the invention.

Cookies

Ingredients	Wt.%
Sugar (granulated)	27.51
Vegetable Shortening	13.54
Salt	0.44
Sodium bicarbonate	0.53
Dextrose solution. (4.0% in water)	10.37
Flour (unbleached, AP)	47.61
Total	100.00

Chocolate cookies

Ingredients	Wt.%
Sugar (granulated)	26.51
Vegetable Shortening	12.54
Salt	0.44
Sodium bicarbonate	0.53
Dextrose solution. (4.0% in water)	10.37
Flour (unbleached, AP)	46.61
Cocoa powder	3.00
Total	100.00

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Cheese crackers

Ingredients	Wt.%
Flour (unbleached, AP)	49.14
Sugar	2.45
NFDM	0.82
Starch (*Baka-Snak*®)	2.45
Inactive Dry Yeast	0.49
Block cheddar	10.00
Salt	0.82
Baking soda	0.29
Monocalcium phosphate	0.65
Vegetable Shortening	8.18
Annatto Extract (*Warner*) 2.7%	0.16
Savoury Flavor 570593*	0.40
Ammonium Bicarbonate	0.98
Water	23.17
Total	100.00

*Firmenich SA

Butter crackers

Ingredients	Wt.%
Flour (unbleached, AP)	54.82
Sugar	2.74
NFDM	0.91
Starch (*Baka-Snak*®)	2.74
Inactive Dry Yeast	0.55
Salt	0.91
Baking soda	0.32
Monocalcium phosphate	0.73
Vegetable Shortening	9.14
Ammonium Bicarbonate	1.10
Water	26.04
Total	100.00

The cookies were packed packed in Ziploc® type bags (low density polyethylene) and kept at room temperature. After 2 weeks of storage and sensory evaluation, they were packed in heat sealed aluminum foil pouches until 10 weeks of age and subjected to a second sensory evaluation.

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Sensory Evaluation Results

Two sensory tests were conducted at 2 weeks and 10 weeks after baking with a 30 person consumer-model sensory panel on key attributes such as overall flavor intensity, flavor intensity while chewing, flavor intensity after swallowing and overall flavor preference. The test was performed using a balanced random block design and the panel response was recorded on 0-10 point scale. The data was statistically analyzed by using Analysis of Variance.

In all these blind evaluation tests the results were the same: the cookies and crackers containing the flavors encapsulated by the method of the invention were judged to perform consistently better than those containing iso-amounts of flavor in liquid or conventionally spray dried form, and this in all the sensory attributes mentioned above, showing that the flavored capsules of the invention constitute prime flavor systems for bakery applications.

Example 17

Preparation of perfume containing capsules according to the invention

Perfume containing capsules were prepared using the following ingredients:

Ingredient	Parts by weight
Capsul® from National Starch	746
Lavander perfume from Firmenich	450
Native Corn Starch Type B from Roquette	10

Procedure:

The solids were dissolved in 1196 parts of water and the perfume to be emulsified into this solution using a high shear rotor/stator homogeniser.

Spray-drying of this perfumed emulsion was performed according to the invention as described in Example 1 using air at 150°C inlet temperature as the hot gas. Using a spray nozzle, the emulsion feed was sprayed in such a way that coarse droplets were formed. These droplets fell into a cloud of Native Corn Starch chosen for its dehydrating and

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anticaking properties. The powder was "caught" in flight by the wet emulsion droplets and created a protective layer, preventing them from sticking together or onto the chamber wall of the spray-drier. At the bottom of this chamber the powder-coated droplets were collected and dried to give final dry beadlets.

The resulting perfumed granules contained 25.5% of Lavender perfume, determined by steam distillation. Bulk density of the granules was measured at 0.500 g/ml and explosivity was measured at 103 bar x m/s (KST) giving a dust hazard class of ST-1. Average particle size of the granulated perfume was determined at 250 microns.

Example 18

Hygroscopy of granulated perfume

Hygroscopicity (the tendency to absorb water) of the granulated perfume was determined in a Dynamic Vapor Sorption, commercialised by Surface Measurements Systems Ltd, 3 Warple Mews, Warple Way, London, W3 ORF, at increasing relative humidity (40%, 50%, 60%, 70%, 80%, 90%) to determine the so-called "melting" point of the two powders at 37°C, as well as the difference in weight of the powder which is placed on a balance in the humidity chamber.

The "melting point", in the context of the present example refers to the relative humidity at which a powder has absorbed so much water that it loses its powdery aspect and starts to flow like a liquid, that is, it "melts". The specific relative humidity at which this happens can be determined by the weight-loss observed via the release of the encapsulated volatile perfume.

The encapsulated perfume is placed on a balance inside a chamber where the relative air humidity is increased every two hours by 10%, starting from 40% relative humidity. Initially, the exposed sample of microencapsulated perfume increases in weight due to the water-uptake as the humidity increases. If the microencapsulated perfume or flavour remains a powder and does not "melt", its weight will remain constant over the two hours at constant humidity. If the microencapsulated perfume starts "melting", the encapsulate is no longer protected inside the capsule matrix, starts evaporating the chamber and the consequent weight loss of the powder is observed.

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The granulated perfume of Example 17 was thus tested according to this method and did not "melt" even at a relative humidity of 90%. The analysis showed that the granulated perfume remained stable even at elevated humidity.

Example 19

Fragrance release of granulated perfume in laundry powder detergent

A detergent composition was prepared by mixing 7.8 parts sodium dodecyl benzene sulphonate, 4 parts of Dobanol® 45-7 (linear primary alcohol ethoxylate C14-15 7EO), 21 parts sodium carbonate, 30.2 parts Zeolite A, 12 parts sodium sulphate and 25 parts sodium perborate. This composition is a base for a detergent powder composition.

To 110 g of the detergent composition above, there was added 1.000 weight % of the granulated perfume of Example 17, containing 25.5% of encapsulated Lavender perfume, to prepare a detergent according to the invention.

In a comparative detergent, an iso-amount of Lavander perfume encapsulated via a conventional spray-drying process were added to 110 g of the detergent composition.

Both detergent samples were stored at 37°C and 70% relative humidity for 1 month in a closed paper box. Then a wash was carried out with both aged detergent samples in a conventional automatic washing machine (Miele® Professional WS 5425) of the front loading type at 95°C with a 2.5 kg load of terry cotton towels. The freshly washed terry cotton towels were evaluated on a blind test by 40 panelists for their olfactive strength and 35 of the 40 panelists found the scent of the terry towels washed with detergent containing granulated perfume according to the invention far stronger when compared to that of the terry towels washed with detergent containing the conventionally encapsulated perfume.
In fact, it was observed that the capsules according to the present invention showed a slower dilution rate in the washing medium than those obtained by a classical spray-drying process, the perfume being thus presumably better retained and thus transferred in larger amounts into the textiles treated with the perfumed detergents.

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Example 20

Preparation of perfume containing capsules according to the invention and use thereof in soaps

A. Perfume containing capsules were prepared using the following ingredients:

Ingredient	Parts by weight
PVOH* (polyvinyl alcohol)	519
Perfume from Firmenich**	410
Sucrose	70
Antifoam	1

* ERKOL® V03/140; origin: ACETEX EXPERIMENTAL.

** Perfume having a floral, citrus, fruity, green, musky and woody character.

Procedure:

The solids were dissolved in 2000 parts of water and the perfume to be emulsified into this solution using a high shear rotor/stator homogeniser.

Spray-drying of this perfumed emulsion was performed according to the invention as described in Example 1 using air at 150°C inlet temperature as the hot gas. Using a spray nozzle, the emulsion feed was sprayed in such a way that coarse droplets were formed. These droplets fell into a cloud of Native Corn Starch chosen for its dehydrating and anticaking properties. The powder was "caught" in flight by the wet emulsion droplets and created a protective layer, preventing them from sticking together or onto the chamber wall of the spray-drier. At the bottom of this chamber the powder-coated droplets were collected and dried to give final dry beadlets.

The resulting perfumed granules contained 25.9% by weight of perfume and 20.7% by weight of native starch.

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B. Soap base formula

A standard tallow base ROZ96/01 (PRISAVON 9250, Uniqema, the Netherlands) was used, having the following composition:

Component	% by weight
Total fatty matter: mixture of Sodium Tallowate and Sodium Palm Kernelate	79.5-82.5
Water	10-13
NaCl	0.3-0.5
Glycerine	0.2-0.4
Free alkalinity	0.01-0.05

C. Preparation of soap bars with capsules

A control soap was prepared by mixing the oil fragrance at 1% by weight in the standard soap base in a stainless steel bowl with a plastic spatula. After absorption for 10 or 15 minutes the soap was extruded twice between 35°C and 40°C to obtain a homogeneous and compact soap slug. The soap slug was cut and the soap stamped, wrapped in a polyethylene film on a RMT press with the 50g stainless rectangular mould.

Soap bars containing the perfumed capsules according to the invention were prepared in the same manner by mixing the powder in the soap base in the amount required to obtain 1% by weight of fragrance in the soap fragrance.

D. Evaluation and results

The olfactive evaluation of the soap bars was done by experts on blind tests and showed that the soap bars containing the perfumed capsules performed significantly better than bars perfumed with just liquid oil, the perfume diffusion and blooming effect upon use having been judged better, when compared to the control soap bars containing just liquid oil.

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Claims

1. A process for preparing capsules having an average diameter in the range of 100 to 2000 µm and containing an encapsulated flavour and/or fragrance ingredient or composition, the process comprising the steps of

- a) preparing an aqueous solution, suspension and/or emulsion comprising said flavour and/or fragrance ingredient in a dissolved, suspended and/or emulsified form, matrix materials and water,
- b) dispersing the emulsion in the form of drops having a mean diameter of 100 to 2000 µm into a spraying tower,
- c) introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower to obtain a coating of powdering agent on the drops of the sprayed emulsion,
- d) supplying, simultaneously to the dispersing step, a hot gas into the spraying tower, and,
- e) removing the powdering agent coated capsules from the spraying tower,

the process being characterized in that the hot gas is supplied in step d) at a temperature in the range of 130-250°C.

2. The process of claim 1, wherein the temperature of the hot gas is above 150°C.

3. The process of claim 1, further comprising the step of intercepting the capsules by a fluidised bed, once they have been coated by the powdering agent and at least superficially dried by the hot gas in the spraying tower.

4. The process of claim 3, in which the fluidised bed is supplied with a gas having a temperature in the range of 40 to about 100°C.

5. The process of claim 1, in which the emulsion comprising the ingredient, matrix components and water has a dry-matter content in the range of 45–80 wt.%, relative to the total weight of emulsion.

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6. The process according to claim 1, wherein ingredient to be encapsulated comprises at least 10 wt.% of chemical compounds having a vapour pressure of or above 0.007 Pa at 25°C.

7. The process of claim 1, in which the obtained capsules have a flavour and/or fragrance ingredient load of 18-50 wt.%.

8. The process according to claim 1, in which the matrix materials comprise polysaccharides, and, in addition saccharides selected from the group of mono- and/or disaccharides.

9. The process according to claim 1 or 8, in which the powdering agent is selected from the group consisting of starch, starch derivatives, talc, bentonite, silicon dioxide, calcium, magnesium, aluminium or potassium silicates, sodium, potassium or calcium aluminosilicates, calcium, sodium, or magnesium carbonates, calcium or magnesium phosphates, ferric ammonium citrate, microcrystalline cellulose and cellulose derivatives or fibers, aluminium, calcium, sodium, magnesium, potassium or ammonium salts of fatty acids, magnesium oxides, and mixtures comprising two or more of the aforementioned powdering agents.

10. The process of claim 9, in which there are obtained capsules having a coating of powdering agent which accounts for 0.1 to 30 wt.% of the total weight of the capsules.

11. The process according to any one of claims claim 1 to 10, wherein the ingredient is selected from the group consisting of a flavour and/or fragrance compound or composition, a flavour or fragrance natural extract, and mixtures thereof.

12. The process according to claim 1, which is carried out in a multi stage drying apparatus.

13. Capsules obtainable by the process according to any of claims 1 to 12, comprising an encapsulated flavour and/or fragrance ingredient.

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14. Capsules having an average diameter in the range of 100 to 2000 µm comprising an encapsulated flavour and/or fragrance ingredient, the load of the ingredient being in the range of 18-40 wt.%, the capsules further comprising a coating provided by a powdering agent, whereby the coating provides 0.1 to 30 wt.% of the total weight of the capsules.

15. Capsules according to claim 13 or 14, having an average diameter comprised between 200 and 800 µm, and more preferably between 300 and 500 µm.

16. Capsules according to claim 15, having an average diameter of about 350 µm.

17. Capsules according to claim 13 or 14, having a coating of powdering agent, wherein said powdering agent is selected from the group consisting of starch, starch derivatives, talc, bentonite, silicon dioxide, calcium, magnesium, aluminium or potassium silicates, sodium, potassium or calcium aluminosilicates, calcium, sodium, or magnesium carbonates, calcium or magnesium phosphates, ferric ammonium citrate, microcrystalline cellulose and cellulose derivatives or fibers, aluminium, calcium, sodium, magnesium, potassium or ammonium salts of fatty acids, magnesium oxides, and mixtures comprising two or more of the aforementioned powdering agents.

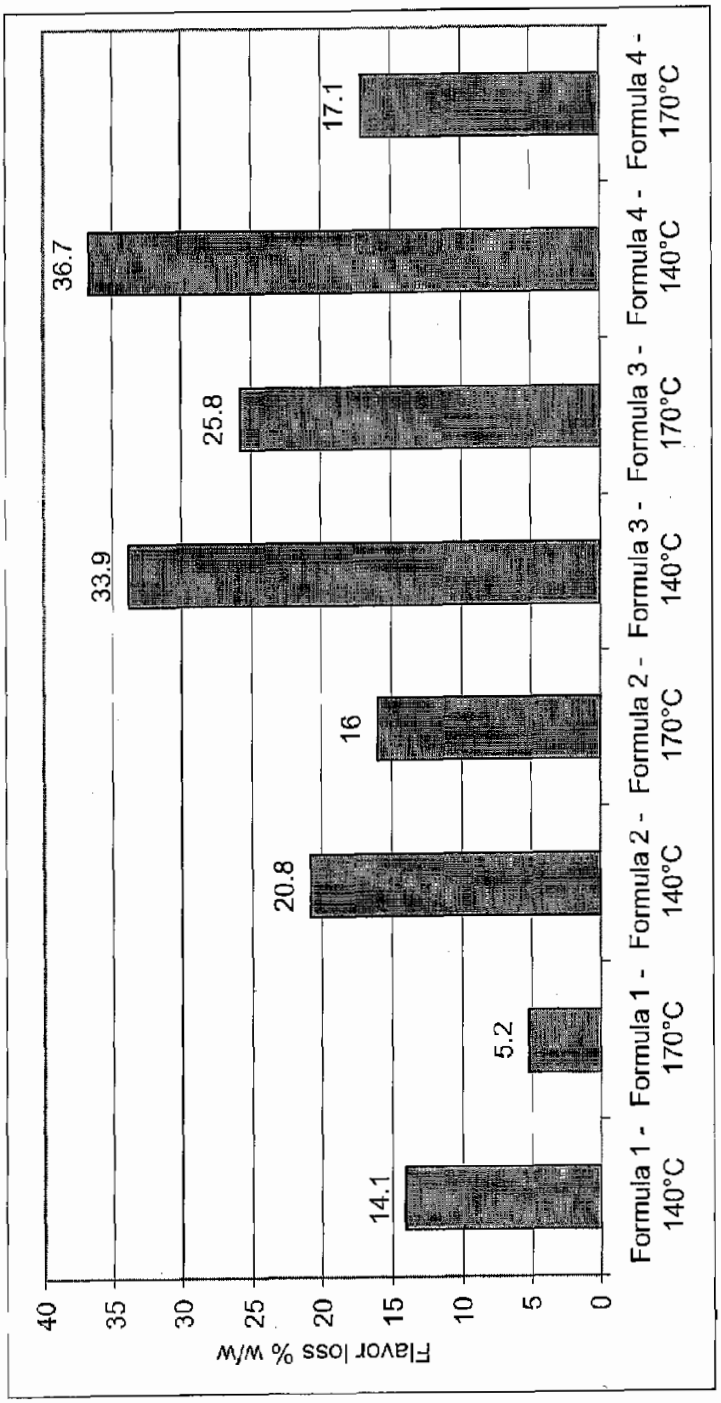
18. A product comprising the capsules according to any one of claims 13 to 17.

19. A product according to claim 18 which is a food or a chewing gum, a soap, a powder detergent or a cosmetic preparation.

20. A method for reducing loss of flavour and/or fragrance ingredient during the preparation of capsules having an average diameter in the range of 100 to 2000 µm, the process comprising the step of dispersing a suspension and/or emulsion comprising the flavour and/or fragrance ingredient, matrix materials and water into a spraying tower, whereby the spraying tower is further supplied with a hot gas having a temperature in the range of 121 to 250°C and whereby simultaneously a powdering agent is introduced into the spraying tower.

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Figure 1



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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2006/054008

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/22 A23L1/00 B01J13/04 A61K8/11

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Minimum documentation searched (classification system followed by classification symbols)
A23L B01J A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, FSTA, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2006/054008

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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International application No
PCT/IB2006/054008

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(74) Agent: **SALVATERRA-GARCIA, Maria de Lurdes**; Firmenich SA, Rue de la Bergère, 7, P.O. Box 148, CH-1217 Meyrin 2 (CH).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PREPARATION OF POWDERS FROM SLURRIES OF FRAGRANCED AMINOPLAST CAPSULES

(57) Abstract: A process for the preparation of powder products via spray-drying, in a generally known manner, of aqueous dispersions, or slurries, of aminoplast microcapsules comprising an encapsulated oil, wherein, prior to being submitted to spray-drying, there is added to said slurry a de-tackifying colloid in an appropriate amount and the pH of the slurry thus obtained is adjusted to a value comprised between 4 and 6 by means of an acid. This process makes it possible to obtain powders that are particularly useful to impart pleasant and useful properties, namely fragrance and antibacterial or malodor counteracting properties, to consumer products wherein the incorporation of aqueous media or compositions is undesirable and affects the physical structure of the consumer product.

WO 2007/096790 A1

PROCESS FOR THE PREPARATION OF POWDERS FROM SLURRIES OF FRAGRANCED AMINOPLAST CAPSULES

Technical Field

The present invention relates to the perfume and consumer product industries. It concerns more particularly a process for producing powders out of slurries of aminoplast, and more particularly melamine-formaldehyde, capsules containing fragrances and other hydrophobic materials. The invention also relates to the powder products thus obtained, which have novel physical and chemical characteristics, and to the use of such powders in consumer products. The consumer products containing such powders of melamine-formaldehyde capsules are also an object of the invention.

Background Art

The literature is rich in reports of the use of melamine-formaldehyde resins for the encapsulation of active substances and mentions in particular the potential use of such encapsulation systems in perfumery and cosmetic applications. Therefore, amino resin based capsules, also commonly designated as aminoplast capsules, are the subject of a variety of literature reports and patent applications relating to the perfumery and cosmetic industries. In practice, these polymers are capable of forming a protecting shell around the active ingredient that one wishes to protect, thus providing an encapsulation system characterised by its water-insolubility. The active ingredient protected by the capsule may be released through mechanical rupture of the microcapsules, which become brittle when dry.

Some of the typical examples of this type of applications can be found in the following patent documents, but the person skilled in the art will no doubt have knowledge of many other reported applications of fragranced aminoplast capsules in consumer products.

US 5,137,646 describes coated perfume particles for use in fabric softeners and antistatic agents and US 6,620.777 claims improved deposition of fragranced aminoplast microcapsules on fabric from liquid fabric softeners by adding cationic polymers.

US 4,145,184 claims granular and liquid laundry detergent compositions comprising fragranced microcapsules.

US 6.248,703 discloses soap bar and detergent bar compositions comprising melamine capsules that contain essential oils.

WO 03/089561 describes the use of fragranced microcapsules in fabric refresher aerosols.

The use of such fragranced aminoplast capsules in liquid formulations for household and cosmetic applications is also known for example from US Patent 5,188,754, assigned to Procter & Gamble, which describes detergent compositions containing perfumes in the form of friable microcapsules. US Patent 5,137,646, also to Procter & Gamble, describes the preparation and use of perfumed aminoplast particles which are stable in fluid compositions such as fabric softeners. However, this composition requires a two-step manufacturing process where the perfume is firstly solidified with a meltable polymer, followed by grinding of the solidified perfume and coating with the aminoplast resin.

The technical advantage of such friable aminoplast microcapsules is that they are water insoluble and resistant to heat. As a result, the fragrance or other hydrophobic substance remains fully encapsulated when capsules are dispersed in aqueous formulations and during laundering processes for example. The fragrance is mainly released by mechanical manipulation of the dry target surface such as skin, hair or fabric. A general range of encapsulate concentration, namely fragrance content, of the microcapsules slurry is between 1 and 50%, by weight, relative to the weight of the slurry, the latter also containing typically 4 to 20% by weight of encapsulating shell material in a free form, and the balance being water.

The general process for the preparation of aminoplast microcapsules containing encapsulated fragrances or other hydrophobic materials is also a well-known state of the art and is widely described in the patent literature. Early examples of the latter are represented by US Patents 3,016,308, 3,516,846 and 3,516,941, as well as US 4,396,670 to The Wiggins Teape Group Ltd., and many other more recent patent documents have addressed this subject.

One can also find general literature reviews of such methods as well as of the uses of the microcapsules obtained there-from. For the sake of example there will be cited here the publications K. Dietrich et al. (1989 and 1990), *Amino resin microcapsules,* Acta

Polymerica 40(4), pgs. 243-251, 40(5), pgs. 325-331, 40(11), pgs. 683-690 and 41(2), pgs. 91-95. Another general review of interest is that of H. Y. Lee et al., J. Microencapsulation (2002), 19 (5), pages 559–569.

The person skilled in the art is also referred to recent documents such as International Patent Application WO 2006/018694, belonging to the present Applicant, as well as to US 6,024,943 to Quest International and WO 01/41915 to Microcapsules Technologies, and to the references generally cited in these documents.

The preferred encapsulating shell material is a polymeric shell, which is the reaction product of urea or melamine and an aldehyde, such as formaldehyde. When aqueous slurries of such microcapsules are dried, the water evaporates and the encapsulated fragrance is fully retained in the dried microcapsules.

The micro encapsulation principle is relatively simple. A thin polymer shell is created around droplets or particles of an active agent emulsified or dispersed in a carrier liquid. Preferred polymer materials for the microcapsules shell are those which are capable of polymerisation under acid pH from a water-soluble pre-polymer state. Such pre-polymers are made by reacting urea and formaldehyde in a formaldehyde urea molar ratio of from about 1.2:1 to 2.6:1. Thiourea, cyanuramide, guanidine, N-alkyl ureas, phenols, sulfonamides, anilines and amines can be included in small amounts as modifiers for the urea. These polymers formed from such pre-polymer materials, under acidic conditions, are water-insoluble and can provide the required capsule friability characteristics.

As described in US 4,233,178, microcapsules based on melamine/formaldehyde resins are preferred over those based on urea/formaldehyde resins, because the resulting capsules are more impermeable due to a higher degree of cross-linking of the film-forming resin.

Microcapsules made from the preferred melamine-formaldehyde shell materials can be made by the processes described in WO 01/51197, US 6,261,483, US 2003/0004226, US 4,406,816 and EP 0415273.

In all the known processes, a large part of the obtained capsule slurry is water, and it often desired to eliminate this water and to obtain a dry capsule concentrate.

Although in many cases the capsule slurry can be used, in certain applications, it is preferred to use such aminoplast capsules in a dry form because water disturbs the final structure or composition of the final product into which the microcapsules are

incorporated. Examples are water-free liquid detergents and fabric softeners for example, namely those packaged in water soluble polyvinyl alcohol pouches, hair oils, body oils, hair and body sprays based on cyclomethicone, powder detergents and fabric conditioning sheets typically intended for use in tumble dryers. In this latter case, during the preparation of the dryer sheets water-insoluble esterquats are applied as a hot melt on a non-woven material. These waxes are incompatible with water and have a melting point that is higher than the boiling point of water. Incorporation of aqueous slurries of aminoplast capsules is therefore not possible under such conditions.

Another example of specific applications where melamine microcapsule solids are appropriate is the case of anhydrous liquid detergents which have the technical advantage that they can contain bleach and bleach activators but wherein the latter will react immediately in the presence of water, as described for example in US 4,800,035 or US 5,057,238, to Colgage Palmolive. It is therefore not convenient to add any aqueous emulsions or dispersions to such formulations.

Non aqueous fabric softeners can be formulated on a completely oil-based composition which is then stable in water soluble polyvinyl alcohol packages such as described in US 6,492,315, to Colgate Palmolive. In such water-free bases, it is difficult to incorporate aqueous dispersions of microcapsules because they would readily separate from the formulation and attack the water soluble packaging, possibly causing leaking of the liquid softener during storage.

In all such cases it is therefore required to incorporate the melamine-formaldehyde microcapsules in solid form and the present invention brings exactly an advantageous solution to this problem by providing a process for converting the aqueous slurries into free flowing powders via spray drying of the slurry under well-controlled conditions.

Although the concept of spray drying the slurries has been generally and briefly mentioned for example in US 20040071742 and in WO 2004/016234, no particular details or guidance to the specific process conditions used has been reported in the prior art. We have now surprisingly found that spray drying of the slurries must be carried out under specific processing parameters and using specific carrier materials in order to obtain a free flowing powder of the microcapsules enclosing the hydrophobic perfume or other material.

In fact, we have been able to establish that, under many current spray drying method conditions, encompassed by a general reference or citation of possible spray

drying methods to be applied to such aminoplast capsule slurries, there are not in fact obtained free flowing powders but products wherein the microcapsules tend to agglomerate and deliver unstable materials upon storage.

This is a consequence of the fact that, as mentioned above, aminoplast microcapsules are generally prepared by interfacial polymerization in the presence of emulsifiers. These emulsifiers can be anionic thickeners such as carboxymethylcellulose, gum arabic, polyvinyl alcohol, or combinations of such polymers, with anionic surfactants such as sodium dodecyl sulfate. Such anionic thickeners are not incorporated into the capsule membrane and are still present in the final slurry.

In other approaches, emulsifiers that have no thickening properties are used and they are incorporated into the capsule membrane during the polymerization process. Such emulsifiers are sulfonated copolymers of acrylamide and acrylic acid as described in WO 01/51197. To avoid separation of capsules from the final slurry, thickening polymers need to be post-added, requiring a further processing step to obtain viable powders.

We have now found that, when aminoplast capsules are spray-dried, the thickening polymers strongly disturb the process. During the spray-drying process, the aminoplast capsules form sticky agglomerates and deposits on the inner walls of the spray-dryer because the melamine resin continues crosslinking under the high temperature conditions of the spray drying process. The presence of the thickening polymers in the aminoplast slurry thus promotes further agglomeration of the microcapsules amongst themselves and onto the reactor wall of the spray-dryer. Such deposits cannot be easily washed-off from the reactor walls and mechanical cleaning is required, increasing production time and cost. Moreover, the spray-dried powder is only obtained in small yields of maximum 30% and forms agglomerates and lumps that cannot be easily dispersed into liquid formulations. As a result, aminoplast microcapsules that are prepared according to the processes described in WO 98/28396 and US 5,188,753, for example, cannot in fact be efficiently spray-dried, because of the presence of the anionic emulsifying thickeners required for the encapsulation process.

The present invention provides a process which avoids such problems. The process of the invention allows spray drying of aminoplast microcapsule slurries under specific conditions described hereafter.

Moreover, the process of the invention dispenses with the need to add post-encapsulation thickening polymers to stabilize the aqueous slurry of capsules, thus avoiding their negative impact on the spray-drying process.

We have now found that addition of de-tackifying colloids to aminoplast microcapsule slurries provides a temporary second coating around the microcapsules which inhibits further reaction of the aminoplast resin during the spray-drying.

Water-insoluble inorganic powders such as zeolites, bentonites or silica, can be considered as such de-tackifying colloids, but a disadvantage of the use of such inorganic colloids is their strong thickening properties, rendering the microcapsule slurry difficult to spray-dry. In fact, usually such inorganic flowing agents are rather added to the dry powder after spray-drying in order to increase its flowability.

Other possible de-tackifying colloids are anionic organic polymers, like gum Arabic, or non-ionic organic polymers such as polyvinyl alcohol or alkyl modified cellulose derivatives, as previously cited. Typical examples are ethyl cellulose or hydroxypropyl cellulose. Hydrocarbons and sugars, such as sucrose, mannose, maltose, sorbitol, xylitol or copolymers of sucrose and dextrose known as refined polydextrose (Litesse® from Danisco), or yet dehydrated glucose obtained from hydrolysis of starch (Glucidex® 6 from Roquette), have also been used as de-tackifying agents.

However, due to their lack of emulsification properties, many of such products still allow some agglomeration of the microcapsules during spray drying and need to be added at fairly high quantities in order to reduce the sticky deposits of the capsules on the reactor walls of the spray-dryer to allow easy wash-off thereof with water.

It is thus that, although in WO 2004/016234 to Quest, spray-drying of aminoplast microcapsules in the presence of carboxymethylcellulose is described in example 7, no specific benefit of the use of this water-soluble coating could in fact be found with regard to this microcapsule agglomeration and wall depositing problem. Although the resulting powder is described in this document as being free-flowing, in our own experience such spray-dried powders were sticky and difficult to wash off from the spray-drier.

The present invention provides a process for the preparation of powders from aqueous aminoplast microcapsule slurries, via spray drying the latter using specific materials as spray drying carriers. The process of the invention allows full retention of the encapsulated hydrophobic material, namely fragrance, during the spray drying and makes it possible to improve the odor quality of the aminoplast microcapsules thus obtained.

Disclosure of the Invention

The present invention provides a process for the preparation of powders of aminoplast, and more particularly melamine-formaldehyde, microcapsules containing fragrances or other hydrophobic materials, wherein an aqueous slurry of aminoplast microcapsules, comprising a water soluble organic de-tackifying colloid having emulsifying properties, is spray-dried in a generally known manner. Prior to the spray-drying the pH of the slurry is adjusted to a value comprised between 4 and 6 by means of an acid.

According to a preferred embodiment of the invention, the aminoplast capsule slurry further contains a flame retardant agent. Suitable such agents are described in detail in International patent applications WO 03/043728 and PCT/IB2005/053089, belonging to the present Applicant and the contents of which are hereby included by reference. The use of short chain carboxylic acids, as described therein, is preferred.

The concentration of capsules in the aqueous slurries which are dried according to the process of the invention will be typically comprised between 0.5 and 50% by weight, relative to the total weight of aqueous suspension.

The dry capsules resulting from the process of the invention form a non-sticky powder that is easy to wash-off with hot water from the reactor walls of the spray-drying tower, does not have any amine smell (unlike what is the case with the dried aminoplast microcapsule products prior known) and is free flowing. Moreover, it easily disperses in aqueous and non-aqueous formulations of a variety of liquid consumer products without the help of any dispersing agents. In water, the powder disperses into the original particle size of the microcapsules without the formation of agglomerates, the particle size being fully retained during the spray-drying process.

We have now established that water soluble colloids with emulsifying properties showed excellent de-tackifying performance during the spray-drying process of aminoplast capsules. Addition of such emulsifying colloids strongly increased the final yield of spray-dried powder and allowed easy cleaning of the spray-drier with water. In particular, addition of lipophilised cellulose such as dioctenylsuccinated starch (Capsul® from National Starch), HI-CAP® 100 (hydrogen octenylbutanedioate starch), or of emulsion stabilizing starch derivatives obtained from waxy maize (such as the

commercial products of the type of Purity Gum 2000 from National Starch) to the aminoplast capsule slurry avoided agglomeration and lump formation of the spray-dried microcapsules and allowed easy dispersion of the dried capsules in the end-product liquid formulations into which they were incorporated.

Moreover, the above-mentioned preferred embodiment of the process of the invention is particularly useful for preparing powdered melamine-formaldehyde based microcapsules. This type of microcapsules typically exhale a strong amine smell. We have now been able to completely eliminate this malodor by reducing the pH of the slurry to pH = 5 with an acid such as citric acid, hydrochloric acid or sulfonic acid for example. Surprisingly, we have also established that the acid further improves the emulsification properties of the colloid, namely Capsul®, thus improving the dispersibility of the microcapsule powder thus obtained in liquid formulations.

The emulsifying properties of such modified starch derivatives could be clearly seen in the resulting particle size distribution of the spray-dried capsules. When Capsul® or Purity Gum 2000 were added to the capsule slurry, the spray-dried powder obtained showed a more homogeneous and smaller average particle size, compared to capsules spray-dried in the presence of Litesse® Ultra or Glucidex® 6, which were also tested but did not provide as good results, or required substantially higher amounts to be used to achieve similar results.

According to the invention, a modified starch of anionic character with emulsifying properties is preferred as the detackifying colloid. The modified starch is added to the slurry in an amount comprised between 1 and 10%, and more preferably between 1 and 3% by weight, relative to the weight of the slurry.

The modified starches appropriate for use according to the invention include hydrolyzed starch, acid thinned starch, starch esters of long chain hydrocarbons, starch acetates, starch octenyl succinate, and mixtures thereof.

The term "hydrolyzed starch" is meant to mean here oligosaccharide-type materials that are typically obtained by acid and/or enzymatic hydrolysis of starches, preferably corn starch. Suitable hydrolyzed starches include maltodextrins and corn syrup solids. Starch esters having a degree of substitution in the range of from about 0.01% to about 10.0% are also useful. The hydrocarbon part of the modifying ester should be from a C_5 to C_{16} carbon chain.

Preferably, octenylsuccinate substituted waxy corn starches of various types shall be used, such as:

1) waxy starch: acid thinned and octenylsuccinate substituted;
2) blend of corn syrup solids: waxy starch, octenylsuccinate substituted, and dextrinized;
3) waxy starch: octenylsuccinate substituted and dextrinized;
4) blend of corn syrup solids or maltodextrins with waxy starch: acid thinned octenylsuccinate substituted, and then cooked and spray dried; and
5) waxy starch: acid thinned and octenylsuccinate substituted, then cooked and spray dried

can also be used in the present invention. Commercialized starches that are advantageously used in the context of the invention include the products sold under the tradenames Capsul®, HiCap® and Alcocap®, as well as Purity Gum 2000, all from National Starch.

According to very advantageous embodiments of the process of the invention, there is further added to the microcapsule slurry a flame retardant agent which is intended to allow for reduction of the powder explosivity during the spray drying process and/or during storage thereof.

The flame retardant agents that are appropriate for use according to the invention include all the materials that have been cited in this capacity in the previously cited International patent applications, the contents of which are hereby included by reference. Examples of such ingredients are described in detail in these documents which further disclose the appropriate amounts thereof to be used in spray drying processes.

As the encapsulate in the microcapsules of the invention, there can be used a wide range of water- insoluble materials, amongst which there can be cited flavors and fragrances, antimicrobial or bacteriostatic agents, or yet malodor counteracting agents, and cosmetic/cosmaceutical or nutritional/nutraceutical ingredients. Following preferred embodiments of the invention, will be used fragrance compositions or ingredients, antibacterial or malodor counteracting agents.

Preferred embodiments resort to the use of fragrance ingredients or compositions. By fragrance ingredients or composition it is understood here an ingredient or mixture of ingredients capable of activation an olfactive receptor of a human or animal subject. These are typically mixtures of ingredients capable of imparting a pleasant odor to the

end product into which the microcapsules are incorporated, and the skilled perfumer is able to create such mixtures as a function of the perfuming effect that it is desired to impart and the perfumer's own creative capabilities.

The nature of the fragrance contained in the capsules is therefore immaterial in the context of the invention, provided that it is compatible with the materials forming the capsules. It will be typically chosen as a function of the perfuming effect that is desired to achieve with the dispersion or consumer product of the invention, and it will be formulated according to current practices in the art of perfumery. It may consist of a perfume ingredient or a composition. These terms can define a variety of odorant materials of both natural and synthetic origin, currently used for the preparation of perfumed consumer products. They include single compounds or mixtures. Specific examples of such components may be found in the current literature, e.g. Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming consumer products, i.e. of imparting an odor to a consumer product traditionally fragranced, or of modifying the odor of said consumer product.

Natural extracts can also be encapsulated into the system of the invention; these include e.g. citrus extracts such as lemon, orange, lime, grapefruit or mandarin oils, or essentials oils of plants, herbs and fruits, amongst other.

The prior art is rich in citations of such fragrance compositions and even in reports of allegedly optimised perfumes to be encapsulated, so as to provide stable microcapsules. General rules of perfume creation have been used for a while as evidenced by the contents of earlier patent literature of which the patent publications WO 01/41915 to Microcapsule Technologies, and WO 98/28398 and WO 02/74430 to Quest International are representative examples freely available to the perfumer. All these prior art reports are part of the general knowledge in the art and can be used by the skilled perfumer without particular difficulty and are thus naturally incorporated into the present disclosure by way of reference and citation. A more detailed description of the fragrance compositions that can be used according to the invention is thus not warranted here.

The amount of oil encapsulated in the powders obtained according to the invention varies in a wide range values, typically comprised between 1 and 90% by weight, more preferably between 20 and 80% by weight, relative to the weight of powder.

In addition to the fragranced capsules, the perfuming microcapsules obtained according to the invention may comprise optional ingredients such as antibacterial agents, cosmetic emollients, vitamins, cooling agents, softeners, lubricants, gloss enhancing agents or any other current active ingredient used in cosmetic or household applications, as long as the latter do not alter the capsules.

The invention also relates to the consumer products obtained by incorporation of the microcapsule powders obtained as described above in the final product. Examples are water-free liquid detergents and fabric softeners, namely those packaged in water soluble polyvinyl alcohol pouches, hair oils, body oils, hair and body sprays based on cyclomethicone, powder detergents and fabric conditioning sheets typically intended for use in tumble dryers.

The concentration in which the powder microcapsules of the invention can be added to these products are typically comprised between 0.1 and 10.0% by weight relative to the weight of the product. Such concentrations are given strictly by way of example since their value depends on the perfuming effect desired and on the nature of the product and can be easily adjusted accordingly.

The invention will now be described in further detail by way of the following examples.

Example 1

Preparation of melamine-formaldehyde microcapsule aqueous slurries

a) Fragranced melamine-formaldehyde capsules were prepared by the process described in US 5,162,486. The resulting microcapsule slurry contained 40% by weight of microcapsules, with 32% by weight of encapsulated fragrance. The encapsulated model fragrance POLYNESIA CP 147869 H (woody, floral; origin: Firmenich SA) had a flash point of 97°C.

Such fragranced microcapsules are commercially available under the trade name PopScent® from Firmenich SA.

The capsule's content of the slurry was determined by analyzing the dry solids thereof using a microwave balance from Sartorius (Model MMA 30).

The encapsulated fragrance content was determined by hydro-distillation.

Particle size of the microcapsules in the slurry was around 2 to 3 microns, as determined via a Malvern particle size analyser.

No thickening polymer was added to the slurry. To avoid separation of the microcapsules from the slurry, the dispersion was continuously agitated during the spray-drying process.

b) To the aqueous microcapsule dispersion obtained in a), there was added 0.2%, by weight, relative to the slurry weight, of Tylose® 60'0000, available from Clariant. Tylose® 60'000 is a water soluble, non-ionic thickening polymer (Methylhydroxyethyl Cellulose). The thickener stabilized the aqueous capsule dispersion and no continuous agitation was required in order to keep a homogeneous aqueous dispersion of the capsules.

c) To the aqueous microcapsule dispersion obtained in a), there was added 0.2%, by weight, relative to the slurry weight, of Blanose® from Aqualon.

Blanose® is a water soluble, anionic thickening polymer (refined Carboxymethyl Cellulose). The thickener stabilized the aqueous capsule dispersion and no continuous agitation was required in order to keep a homogeneous aqueous dispersion of the capsules.

d) Fragranced melamine-formaldehyde capsules were prepared as described in a) using, as the encapsulated raw material, Limonene, which has a flash point of 47°C.

Example 2

Preparation of melamine-formaldehyde microcapsule powders

To 100 parts by weight of the slurry of aminoplast microcapsules from Example 1a) there were added 52 parts by weight of a 20% aqueous solution of different modified starches as summarized in Table I below. The blends were neutralized with citric acid (50% aqueous solution) until pH = 5.

The microcapsule aqueous dispersions thus obtained were then spray-dried at Büchi Spray Dryer Model B 290.

The temperature of the incoming air in the spray dryer was 185°C – 190°C, the temperature of the outcoming air 95°C – 105°C. A biphase spray nozzle was used with a nozzle diameter of 0.7 mm.

Table I

	SAMPLE / Parts by weight			
Ingredients	**A**	**B**	**C**	**D**
Example 1a) microcapsule slurry (no colloid)	100	100	100	100
Capsul® (20% aqueous solution)	52			
Glucidex® 6 (20% aqueous solution)		52		
Litesse® Ultra (20% aqueous solution)			52	
Purity Gum 2000 (20% aqueous solution)				52
Citric acid	to pH = 5	to pH = 5	to pH = 5	to pH = 5
	POWDER CHARACTERISTICS			
Yield of spray-dried powder	80%	70%	70%	80%
Weight of encapsulated fragrance	60%	60%	60%	60%
Free fragrance	<1%	<1%	<1%	<1%
Particle size of powder	35 µm	81µm	101µm	28µm
Deposits on walls/Removal	no deposits, easy to rinse with water	no deposits, easy to rinse with water	no deposits, easy to rinse with water	no deposits, easy to rinse with water
Amine smell	none	none	none	none

The addition of Capsul® and Purity Gum to the aqueous slurries resulted in spray-dried powders with a more homogeneous particle size distribution and a much smaller average particle size that those of the powders obtained by adding Litesse® Ultra or Glucidex® to the aqueous dispersions of microcapsules.

Analytical measurements:

The amount of encapsulated fragrance in the dry powder was determined by hydrodistillation.

Particle size of dry powder was determined by laser diffraction from a sample of the un-sieved product. Particle size of the capsule slurry and the powder dispersed in water was determined by laser diffraction with Malvern particle size analyser. The results of the volume weighted average are presented as D[4,3] in microns.

Explosivity was determined by a 20 liter Sphere Apparatus. The 20 liter sphere monitors the evolution of the explosion pressure of fuel/air mixtures in a closed vessel (under vacuum, chemical ignition source of 10 kJ) with time, over a range of product concentrations. This enables determination of the maximum explosion pressure, Pmax, the dust explosion violence, Kst, and the dust explosion hazard class, the ST-class, according to VDI-3673.

The amount of external fragrance on the spray-dried microcapsules was determined by mild extraction of the powder with isooctane for 10 minutes. The centrifuged solvent was injected into a GC-MS spectrometer and the amount of fragrance quantified by comparison to a reference of a 1% by weight solution of the fragrance in isooctane.

Example 3

Preparation of melamine-formaldehyde microcapsule powders

Similar tests to those described in Example 5 were carried out with the ingredients summarized in Table II, in the amounts indicated, using the microcapsule slurries prepared in Example 1.

The dispersions obtained were then spray-dried at Büchi Spray Dryer Model B 290.

The temperature of the incoming air in the spray dryer was 185°C – 190°C, the temperature of the outcoming air 95°C – 105°C. A biphase spray nozzle was used with a nozzle diameter of 0.7 mm.

The results of these tests are summarized in Table II.

Table II

	SAMPLE / Parts by weight							
	Comparative					Invention		
Ingredients	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**
Example 1a) slurry	100					97		
Example 1b) slurry				100				
Example 1c) slurry					100			
Example 1d) slurry		100	100				97	97
Citric acid	to pH 6	to pH 6	to pH 6	to pH 5	to pH 5	to pH 5	to pH 5	to pH 5
Capsul® (20% aqueous solution)						15	15	15
K_3Citrate								2.5
Yield of spray-dried powder	10%	10%	10%	10%	10%	80%	80%	30%
	POWDER CHARACTERISTICS							
Encapsulated fragrance weight	n.d.	n.d.	n.d.	n.d.	n.d.	64%	59%	59%
Free fragrance weight	n.d.	n.d.	n.d.	n.d.	n.d.	0.08%	4%	4%
Comments	powder sticks on reactor walls	powder sticks on reactor walls	powder sticks on reactor walls	powder sticks on reactor walls	powder sticks on reactor walls	no deposit easy to rinse with water	no deposit easy to rinse with water	K_3Citrate causes gel formation but easy to rinse with water
amine smell	strong	strong	none	none	none	none	none	none
Particle size of powder						23 µm	43 µm	27 µm
Particle size of powder dispersed in water						2 - 3 µm		
Explosion violence, Kst	n.d.	n.d.	n.d.	n.d.	n.d.	131 bar m/s	224 bar m/s	93 bar m/s
Explosion hazard class	n.d.	n.d.	n.d.	n.d.	n.d.	ST-1	ST-2	ST-1

n.d. – not determined

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Example 4

Preparation of a Baby Oil Gel containing spray-dried fragranced aminoplast capsules

A baby oil gel was prepared by admixture, in a generally known manner, of the ingredients cited in Table III below, in the proportions indicated.

Table III

Ingredient	Weight %
Part A	
Versagel® M750 (from Penreco)	74.60
Isopropyl Isostearate	13.00
Propylene Glycol Isoceteth-3 Acetate	10.00
Part B	
Isopropyl Isostearate	2.00
Propylparaben	0.10
Part C	
Spray-dried microcapsules of Example 3 L, containing limonene	0.30

The part A ingredients were mixed at 70°C until reaching a uniform mixture. Part B was heated to 60°C until clear. Premixed part B was then added to part A and they were mixed together until obtaining a homogeneous mixture that was then cooled down to 45°C before adding part C to it.

The microcapsules remained homogeneously dispersed in the above formula during a 3 months storage at ambient temperature (around 25°C).

Example 5

Preparation of a Non-Aqueous (water-free) Liquid Fabric Softener containing spray-dried fragranced aminoplast capsules

An anhydrous liquid fabric softener was prepared by admixture, in a generally known manner, in the order and proportions indicated in Table IV below, of the cited ingredients, using the powder microcapsules of Sample L described in Table II of Example 3.

Table IV

Ingredient	Weight %
Polydimethylsiloxane	19.00
Trioleate Glycerol	15.00
Sunflower Oil	60.70
Free Perfume	5.00
Spray-dried microcapsules of Example 3 L, containing limonene	0.30

The above liquid softener formulation was packaged into a polyvinyl alcohol sachet having film thickness of about 0.3 mm. The sachets containing the above formula remained stable during 3 months storage at room temperature and they dissolved rapidly within one to two minutes of starting a wash cycle.

Claims

1. A process for the preparation of powder products via spray-drying, in a generally known manner, of aqueous dispersions, or slurries, of aminoplast microcapsules comprising an encapsulated flavour or fragrance, wherein, prior to being submitted to spray-drying, there is added to said slurry a de-tackifying colloid in an appropriate amount and the pH of the slurry thus obtained is adjusted to a value comprised between 4 and 6 by means of an acid.

2. A process according to claim 1, wherein the acid is selected from the group consisting of citric acid, hydrochloric acid and sulfonic acid.

3. A process according to claim 1, wherein the aqueous slurry further contains a flame retardant agent.

4. A process according to any one of claims 1 to 3, wherein the slurry contains from 0.5 to 50% by weight of microcapsules, relative to the weight of the slurry.

5. A process according to any one of the preceding claims, wherein the aminoplast capsules in the slurry are melamine-formaldehyde microcapsules.

6. A process according to claim 5, wherein the detackifying colloid is a modified polydextrose derivative and preferably dioctenylsuccinated starch or hydrogen octenylbutanedioate starch.

7. A process according to claim 6, wherein the detackifying colloid is added to the slurry in an amount comprised between 1 and 10%, and more preferably between 1 and 3% by weight, relative to the weight of the slurry.

8. A process according to claim 1, 4 or 5, wherein the oil encapsulate is a fragrance or ingredient or composition, an antibacterial or malodor counteracting agent.

9. A process according to claim 5, wherein the encapsulated oil is a fragrance comprising volatile ingredients with flash points lower than 50°C.

10. A process according to claim 1, wherein there is obtained a powder comprising from 1 to 90% by weight of encapsulated oil, relative to the weight of powder.

11. A spray dried powder susceptible of being obtained by the process according to any one of claims 1 to 10.

12. A spray dried powder according to claim 11, comprising from 1 to 90% by weight of a fragrance ingredient composition, relative to the weight of powder.

13. A spray dried powder according to claim 12, wherein said fragrance contains volatile ingredients with flash points lower than 50°C.

14. A consumer product, comprising a spray dried powder according to claim 11.

15. A consumer product according to claim 14, wherein the amount of said powder is comprised between 0.1 and 10% by weight, relative to the weight of consumer product.

16. A consumer product according to claim 14, in the form of a water-free liquid detergent or fabric softener, a hair or body oil or gel, a hair or body spray based on cyclomethicone, a powder detergent or a fabric conditioning sheet.

17. A method to improve the properties, or attractiveness, of a surface such as skin, hair, tile, glass, plastic, concrete or textile surface, which comprises applying to said surface a consumer product according to claim 14 or 16.

18. A method according to claim 16, wherein the odor or cleanliness of said surface is improved or modified.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/050337

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/00 A23L1/22 B01J13/02 C11D3/37 C11D3/50
C11D11/02 A61K8/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L A61K B01J C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/123892 A (PROCTER & GAMBLE) 29 December 2005 (2005-12-29) claims; examples 1-11	1,2,4,7, 8,10-12, 14-18
X	WO 2004/016234 A (QUEST INT) 26 February 2004 (2004-02-26) cited in the application claims; examples 1-7	1,4,5,7, 8,10-12, 14-18
X	EP 0 415 273 A2 (BASF AG [DE]) 6 March 1991 (1991-03-06) cited in the application examples 3,16	1-18
A	WO 03/043728 A (FIRMENICH & CIE) 30 May 2003 (2003-05-30) cited in the application example 3	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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(54) Title: ONE STEP SPRAY-DRYING PROCESS

(57) Abstract: Capsules encapsulating an active or functional ingredient are obtainable by a process in which a feed comprising this ingredient is dispersed in the form of drops in a spraying tower and exposed to a temperature in the range of -20°C to 500°C. In the tower, a cloud of suspended powdering agent provides a coating and prevents the capsules from sticking together and a reactant is provided to react with a polymer or film forming carrier of the active ingredient so as to modify the water solution properties of the capsule walls.

WO 2007/135583 A2

ONE STEP SPRAY-DRYING PROCESS

Technical Field

The present invention relates to a method for preparing capsules having an average diameter in the range of 100 to 2000 μm encapsulating an active ingredient, namely a flavour, fragrance, a functional additive such as a food or nutrition ingredient, an insect repellent or attractant, a pesticide, an antimicrobial or antibacterial agent, dye or antioxidant ingredients, or yet appropriate mixtures of one or more of such ingredients.

The invention further relates to capsules as such, a method for controlling the water dissolution properties of sprayed particles containing an active ingredient and having an average diameter in the range of 100 to 2000 μm, and the use of a multi stage drying apparatus for preparing capsules of the invention.

Background of the Invention and Problem to be Solved

The objective of the present invention is the encapsulation of active compounds and/or compositions in particles having an average diameter of 100 to 2000 μm. Encapsulation, in general, has the purpose of providing a stable, easy to use and process, and transportable, form of active ingredients. If the active ingredient is liquid at ambient temperature, encapsulation within particles has the further advantage of easier handling and mixing with dry products and providing a less concentrated form of the active ingredient, the latter being an advantage in some instances.

Encapsulation in free flowing powders generally has the purpose of creating a form of active ingredients that can be conveniently dosed and mixed with other ingredients or be directly added to consumer end products. In this regard, particle size and load of active ingredient become relevant. Relatively large particles become useless if small quantities of active ingredient are to be added to a consumer end product, because the particle distribution in the product may bring about a significant fluctuation of final concentration in different regions thereof. Relatively small particles, on the other hand, suffer from a less beneficial surface to volume ratio. This ratio is particularly relevant with volatile active ingredients, such as many fragrances and flavours, where loss through evaporation needs to be prevented. Furthermore, the smaller the particles, the higher the risk of explosion of the powder and handling has accordingly to be done more carefully and at a higher cost.

Spray drying has been widely used to encapsulate active ingredients, in particular flavours and/or fragrances, in a glassy matrix and is substantially disclosed in the prior art. In such a process the active ingredient is dissolved or finely dispersed in a water medium comprising a carrier substance susceptible of forming a matrix capable of encapsulating the active ingredient and optionally other ingredients such as emulsifiers, dyes, etc, and this mixture, commonly known as the "feed", is finely sprayed into a chamber where the formed droplets are put in contact with a hot gas, air or nitrogen for example. Water is then evaporated very quickly from the droplets and dry particles ranging from 5 to a couple hundred microns are recovered. These powders contain the active substance finely dispersed in the dry film forming or polymer matrix.

Typically, the drops of the suspension are sprayed through a nozzle in a spraying tower where they are exposed to the hot air, causing the evaporation of water and thus formation of dried particles that are generally collected at the bottom of the drying tower. However, typical spray-drying is not suitable to produce capsules of much higher than about 100 μ diameter, because drying of these large drops would not be sufficiently quick to prevent sticking of the drops to the inner wall of the tower. A further drawback of traditional spray drying methods is the fact that the viscosity of the suspension or emulsion to be spray dried needs to be kept to a few hundred mPas, in order for it to be finely atomized. This restricts the amount of substances such as thickeners that can be added to the suspension or emulsion and/or requires addition of substantial amounts of water. The latter must be removed during the drying step, thus increasing production costs.

Conventional spray drying is therefore not suitable for producing, in one step, particles having a particle diameter in the range of 100 – 2000 μ. If large particles are desired, further steps are needed. In multistage dryers for example, a fluidised bed is integrated at the bottom of the spraying chamber and the fine droplets (less than 150 microns) produced from the nozzle or a rotary atomizer are agglomerated in the chamber to yield agglomerates. These agglomerates are collected in the fluidised bed to finish their drying. The product is then composed of agglomerates of finer primary particles and the maximum size of these agglomerates cannot be larger than 400 microns.

In order to produce big granules of active ingredients or compositions, it is also known to add anti-caking agents into the spray tower during the spraying of the emulsion or suspension. For example, in WO 04/062382 there is disclosed a process for producing

beadlet preparations of fat-soluble substances, wherein an aqueous suspension of a fat-soluble substance is fed into a spray tower while simultaneously introducing powder starch and hot air through separate inlets. This process has a temperature of up to 200°C, but preferably 60-120°C in the spray zone, and the fat-soluble substance is a vitamin, such as vitamins A, D, E, K, a carotenoid, a polyunsaturated fatty acid, an oil or a fat.

WO 91/17821 discloses a process for preparing microcapsules containing a flavourant embedded in a matrix material by spraying an aqueous suspension under the supply of air having a temperature of 50 to 120°C, while simultaneously introducing a spraying agent. The spraying agent may comprise starch, modified starch, tri-calcium phosphate and others. Some examples of this document clearly show that there is a substantial loss of up to 50 wt % of the flavourant material present in the initial emulsion (Examples 1, 3 and 4).

US 4,870,196 describes a method of preparing powdered, free-flowing tocopheryl succinate, wherein a powdering agent of said tocopheryl succinate is present in the spraying zone to facilitate the formation of droplets. The powdering agent is said to "settle" on the tocopheryl succinate as a thin layer thus increasing the size of the particles.

US 4,764,317 discloses a process which includes the production of wet beads that fall onto a layer of powder preventing the beads from sticking together or onto the equipment walls.

Finally, the general idea of using anti-caking agents such as starch to produce large granules of vitamins for example is discussed in the International Encyclopaedia of Food Nutrition, Volume 9, Fat-soluble vitamins, 1970, for example.

In all spray drying or multistage drying processes of this type, the anti-caking agent is added to form a non-reactive coating around the droplets of feed. The size of the feed droplets is increased by a layer of anti-caking agent, but the encapsulating matrix of film-forming or polymer carrier is not modified by this coating.

Therefore, if one desires to obtain particles with slower dissolution rate in aqueous media, a further process must be added in a second step to coat the particles for instance with a wax or a fat to delay their solubility, or to provoke reaction of the particles react with chemical ingredients susceptible of modifying the matrix.

The aim of the present invention is to provide a more cost-effective spraying process, in particular a spray-drying process, wherein a single step allows the production of large particles (between 100 and 2000μm size) of active ingredient having properties

that, as regards dissolution rate and release of the active ingredient, are adapted to application needs. To this effect, the invention provides a one step effective process wherein the matrix is chemically or physically modified during spray drying or spray cooling of the emulsion or suspension of the active/carrier mixture thanks to the addition of a powdering agent, together with a solid or liquid substance susceptible of inducing modification of the carrier matrix, particularly gellation, crystallization, cross-linking or polymerisation of the matrix. The modification or dissolution properties of the matrix may also occur while re-hydrating the capsules in a final application for example.

The process of the invention makes it possible to obtain particles that have diameters larger that 300 μm, the larger particle size obtainable by prior disclosed spray drying methods, whilst being more cost effective than alternative granule forming types of processes, such as extrusion or coacervation methods, or yet agglomeration techniques.

In other particle forming technologies, such as extrusion technologies with twin screw extruders, the amount of water and the residence times in the extruder are insufficient (in particular for volatile ingredients encapsulation) to permit a proper hydration of any substance capable of reacting with the matrix material and/or proper reaction of the matrix polymer with such a reactant. Moreover, particle diameters between 300 to 800 microns are difficult to obtain. In addition, if any reaction were allowed to occur between a reactant and the matrix, the pressure in the extruder would likely increase to unacceptable values and lead to a de-phasing of the flavour or to expansion of the melt at the die exit.

Other technologies, like vibrating or submerged nozzles, are more expensive than the process of the invention due to a low production capacity for particles below 1000 microns and/or require additional operation units like separation from the bath, washing of the beads and separate drying. Furthermore these operation units are detrimental for example to the flavour or fragrance retention and quality.

Coacervation technologies cannot handle both hydrophilic and hydrophobic actives, nor solid materials. Moreover, coacervation requires an additional drying step that is difficult to achieve and affects the retention of volatiles. Coacervation is also not flexible in terms of choice of the polymer shell material.

Finally, fluidized bed spray granulation or spray agglomeration is also more costly and would not allow the production of similar powders as those of the present invention in a single step process.

Summary of the Invention

Accordingly, the present invention provides a process for preparing capsules having an average diameter in the range of 100 to 2000 µm and containing an active ingredient, the process comprising the steps of

a) preparing a solution, suspension and/or emulsion comprising the active ingredient, a carrier or matrix material and a solvent to form a feed;

b) spraying the feed in the form of drops having a mean diameter of 100 to 2000 µm into a spraying tower,

c) introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower;

d) supplying, simultaneously to the spraying step, a gas having a temperature in the range of –20°C to 500°C into the spraying tower; and,

e) removing the capsules from the spraying tower;

wherein, simultaneously with the addition of the powdering agent used in step c), there is introduced into the spraying tower a substance capable of reacting with said carrier material to modify the dissolution properties of the obtained capsules in aqueous media.

In most preferred embodiments of this process, the solvent is a water-based solvent, and preferably water.

According to particular embodiments of the process of the invention, the latter is a spray-drying process wherein a hot gas is supplied into the spraying tower, at a temperature of 50°C to 500°C, more preferably above 120°C, in step d) of the process. Surprisingly, in spite of the use of such high temperatures, the loss of volatiles encapsulated according to this embodiment was significantly lower than in prior known spray drying processes wherein lower hot air temperatures were employed.

In such spray drying embodiments of the process, the temperatures of the hot air are advantageously in the range of 100°C to 250°C, and most preferably in the range of 120°C to 200°C.

Other aspects of the invention, relate to spray-cooling processes, i.e. processes wherein the air supplied in step d) is at a temperature not above 30°C, more preferably between –20°C and 10°C.

In other particular and preferred embodiments of the process of the invention, the powdering agent comprises the substance capable of reacting with the carrier material of the feed.

Specific embodiments of the process relate to a multistage spray drying or spray cooling process wherein the formed particles are collected in a fluidised bed drier or cooler provided at the bottom of the spraying chamber. Optionally, a second drying or cooling device may be integrated thereafter to allow more precise control of the drying or cooling of the particles.

The present invention also provides particles obtainable by the above-mentioned process and the use of such particles in consumer products traditionally improved or modified by means of flavouring or perfuming ingredients, nutritional supplements such as vitamins or polyunsaturated fatty acids, antioxidant or antibacterial agents, dyes and other substances have a functional purpose.

Preferably, the present invention provides capsules having an average diameter in the range of 100 to 2000 μm encapsulating a flavour and/or fragrance ingredient, the load of the ingredient being in the range of 18-50 wt %, preferably 20-40 wt %, the capsules comprising a coating provided by a powdering agent, whereby this coating provides 0.1 to 30 wt % of the total weight of the capsules.

The present invention further provides a method for controlling the water dissolution properties of sprayed particles containing an active ingredient and having an average diameter in the range of 100 to 2000 μm, wherein the particles are prepared according to the process described above.

In another aspect, the present invention provides the use of a multi stage drying apparatus for preparing capsules according to the method of the present invention.

The process of the present invention entails a number of important advantages over the processes known from the prior art. First of all, it is a one step, low cost process, allowing the production of large particles and tolerating spray drying or cooling of formulations having higher viscosity an a stickier texture than those used in prior art spraying processes. The obtained solids provide a better control of the active ingredient release as they can be designed to have a variety of water solubility behaviours, from being insoluble, to being partially or slowly soluble, or yet characterized by very fast solubility in aqueous media. Moreover, the obtained particles can have dense walls,

unlike what is the case of agglomerates. It was also observed that the particles were on average more spherical.

Description of the figures

Figure 1 shows dry granules obtained according to the invention.

Figure 2 shows the particles of Figure 1 after residence in water for 30 minutes at 50°C.

Description of Detailed Embodiments of the Invention

The present invention provides a process as recited above for preparing capsules having an average diameter in the range of 100 to 2000 µm encapsulating an active ingredient.

By an "active ingredient" it is meant throughout this description any individual ingredient or mixture of ingredients capable of being encapsulated in a matrix such as described here-below via a spray drying or spray cooling process and providing a functional effect of the flavouring, perfuming, pharmaceutical, nutritional, cosmetic, cleaning, antibacterial or deodorizing, antioxidant or yet softening type, intended for use in a consumer product.

This designation shall include in particular flavours and/or fragrances, meaning ingredients capable of imparting or modifying the odour and/or taste and texture properties of solid or liquid consumer products traditionally perfumed and/or flavoured, such as perfumes, soaps, cosmetics and other body care products, hair care products, foods or beverages, chewing gums or oral care products such as mouthwashes and toothpastes, or yet pharmaceuticals, food supplements and other such products.

The expression "active ingredient" also includes materials other than flavours and fragrances, which can be advantageously encapsulated according to the invention and thus entrapped in a glass matrix. Examples are functional additives such as sugar replacement materials, pharmaceuticals, vitamins and diet or nutritional supplements and therapeutic agents. In particular, ingredients such as polyunsaturated fatty acids, or commercial oils rich in such acids, which will remain stable and retain pleasant taste in the capsules of the invention.

Antioxidants and vitamins, for example, ascorbic acid (vitamin C), tocopherol (vitamin E), or mixtures thereof, are also "active ingredients" in the context of the

invention, as are any other common nutritional or cosmaceutical and food ingredients that may generally benefit from encapsulation according to the process of the invention.

Moreover, deodorizing, malodour-counteracting and antibacterial or antimicrobial compounds and compositions, traditionally employed in body or air deodorants or in the preservation of food and cosmetic products, are also "active ingredients" according to the invention.

The "active ingredient" according to the invention further comprises therapeutically active and pharmaceutical ingredients.

The process of the present invention may be performed in any conventional spraying tower such as described for example in WO 2004/062382 (in particular on page 2, lines 26-35). A conventional multi-stage drying apparatus is quite appropriate for conducting the steps of this process. It comprises a spraying tower, and, at the bottom of the tower, a fluidised bed intercepting partially dried particles after falling across the tower. In a typical multi-stage drier, an air inlet and an air outlet are located in the upper region of the tower. Generally, it is possible to maintain, in these devices, a suspension or cloud of fine particles, herein referred to as a "powdering agent", as is required for the purpose of the present invention. The powdering agent is generally introduced by a separate inlet that may preferably be situated either close to the inlet of the aqueous emulsion or in the lower part of the drying tower. The powdering agent is, in the operation mode, in constant movement and may exit the tower together with the air outlet to be returned back into the same tower.

The capsules produced according to the present invention have an average diameter in the range of 100, and more preferably 200, to 2000 µm. Preferably, the average diameter is in the range of 200 to 800 µm, more preferably from 300 to 500 µm. The term "average" and/or "mean" as used for example in the expression "average diameter" refers to the arithmetic mean.

The size of the capsules is determined by the size of the drops that are dispersed into the drying tower according to a step of the method of the invention. According to an embodiment of the invention, the starting emulsion or suspension of active ingredient and carrier or matrix material, i.e. the feed, is guided through a spraying nozzle or through a centrifugal wheel disk into the spraying tower. Other devices may be used to disperse the feed into the form of droplets of a controlled average size. For instance, vibrating orifices may be used instead.

If a spraying nozzle is used for dispersing the drops, their size may be controlled by the flow rate of an atomising gas introduced through the nozzle, for example. When a centrifugal wheel disk is used for dispersal, the main factor for adjusting droplet size to the terms of the present invention is the centrifugal force with which the drops are dispersed from the disk into the tower. The centrifugal force, in turn, depends on the speed of rotation and the diameter of the disk. The feed flow rate, its viscosity and surface tension, as well as the disk geometry, are also parameters controlling the final drop size and size distribution. By adjusting these parameters, the skilled person can control the size of the drops of the composition to be dispersed in the tower.

The process of the present invention preferably comprises the step of preparing an aqueous solution, suspension and/or emulsion, commonly designated as the feed, comprising water, the active ingredient, the matrix materials and possibly an additional reactant capable of modifying such matrix material by reacting with the reactant present in the powdering agent.

Within the context of this specification the word "comprises" is taken to mean "includes, among other things". It is not to be construed as meaning "consists only of".

The active ingredient, typically a flavour and/or fragrance, may thus be mixed with a carrier system by dissolving it together with a polymer or other matrix material, by suspending and/or by emulsifying it therein. For the sake of convenience, the term emulsifying is used to encompass all the different forms of mixing the active ingredient with the matrix materials.

The active ingredient may be hydrophilic and/or hydrophobic. Accordingly, the invention is applicable to a large family of ingredients including water soluble ones, such as juices or reaction flavours, for example. The ingredient may also comprise a combination of hydrophilic and hydrophobic components. If the ingredient is hydrophilic, it will generally be dissolved in the aqueous solution together with the matrix materials. According to a preferred embodiment, the ingredient comprises hydrophobic components, while the matrix materials may be soluble in water. Generally, in this case, the hydrophobic ingredient is emulsified in the form of small droplets having an average diameter in the range of 0.5-10 µm, preferably 1-5 µm for example, within the matrix materials. Emulsification may be made, for example, by using a high pressure homogeniser or a colloid mill, preferably in the presence of an emulsifier

Flavour and/or fragrance active ingredients or compositions encompass ingredients of current use in the flavour and/or fragrance industry, of both natural and synthetic origin. It includes single compounds and mixtures. The capsules used in the invention can encapsulate volatile or labile ingredients in liquid form, preferably with a log P in the range of -2 and 7, preferably 2 - 6. Specific examples of such components may be found in the current literature, e.g. in Fenaroli's Handbook of flavour ingredients, 1975, CRC Press; Synthetic Food adjuncts, 1947 by M.B. Jacobs, edited by Van Nostrand; or Perfume and Flavour Chemicals by S. Arctander, 1969, Montclair, New Jersey (USA).

Accordingly, in a preferred embodiment, the ingredient is selected from the group consisting of a flavour and/or fragrance compound or composition, a flavour or fragrance natural extract, and a mixture of any of the before mentioned ingredients.

Flavour and/or fragrance ingredients are well known to a person skilled in the art of aromatising and/or providing a pleasant odour to consumer products, i.e. of imparting an odour or a flavour or taste to a consumer product, or of modifying the taste and/or odour of said consumer product. Natural extracts can also be encapsulated into the system for flavouring or perfuming consumer end products. Examples of these include, amongst others, citrus extracts such as lemon, orange, lime, grapefruit, or mandarin oils or coffee, tea, mint, cocoa or essential oils of herbs and spices.

Other examples of flavour and/or fragrance active ingredients are synthetic flavour and/or fragrance oils, flavouring aromatics and natural extracts such as oils, essential oils, oleoresins and other extracts derived from plants, for example from leaves, flowers, fruits, roots, rhizomes, stem, and so forth.

Flavours included by the term flavour ingredient are reaction flavours, or processed flavours. These flavours may be obtained by heating food ingredients and/or ingredients appropriate for use in foodstuffs or in processed flavourings. A nitrogen source and a carbohydrate source are necessary to perform a Maillard type reaction for obtaining such processed flavours.

The terms flavour and fragrance also include compounds such as cooling, refreshing, salivating, pungent, tingling and hot/spicy compounds of current use in fragrances and flavours.

The flavour and/or fragrance ingredient may be present in the form of a mixture with solvents, adjuvants, additives and/or other components, generally those of current use in the fragrance and/or flavour industry.

A typical characteristic of flavour and/or fragrance ingredients is the high proportion of volatile compounds and/or components. Accordingly, in an embodiment, the ingredient comprises at least 10 wt %, preferably at least 20 wt %, more preferably at least 30 wt % and most preferably at least 40 wt % of chemical compounds having a vapour pressure of ≥ 0.007 Pa at 25°C. Preferably, at least 10 wt % have a vapour pressure of ≥ 0.1, more preferably, at least 10 wt % have a vapour pressure of ≥ 1 Pa at 25°C, and most preferably, at least 10 wt % have a vapour pressure of ≥ 10 Pa at 25°C. The value of 0.007 Pa at 25°C is selected because it encompasses most of the compounds used by the skilled flavourist and/or perfumer. Compounds meeting these criteria are generally regarded as having a volatile character. In addition, compounds that remain odourless due to a lower volatility are excluded. The limit of 10 wt % of such highly volatile compounds is regarded as being a substantial part of the active flavour or fragrance ingredient that can be encapsulated according to prior known spray drying processes.

For the purpose of the present invention and for the sake of convenience, the vapour pressure value is determined by calculation. Accordingly, the method disclosed in "EPI suite"; 2000 U.S. Environmental Protection Agency, is used to determine the concrete value of the vapour pressure of a specific compound or component of the active ingredient.

In the context of the present invention, percentages are percentages by weight of dry matter, unless otherwise indicated. Similarly, if proportions are indicated as parts, parts of weight of dry matter are meant. Where water is indicated as part of a composition, percentages refer to the total weight of the composition, including water.

Matrix materials useful in the preparation of the feeds in a step of the present invention have the purpose of providing a carrier for the active ingredient. Preferably, the matrix materials are selected on the basis of their capacity to form a film or a glassy matrix upon the drying of the feed dispersed drops. A glassy matrix is an amorphous solid characterized by viscosities of the order of about 10^{10} to 10^{12} Pa*s and an extremely low molecular mobility. A good understanding of the glassy state is provided by Dominique Champion *et al* in "Towards an improved understanding of glass transition and

relaxations in foods: molecular mobility in the glass transition range", Trends in Food Science and Technology 11 (2000) 41-55.

Matrix components may be selected, for example, from polymers, namely proteins and pectin in particular, a very convenient material in food supplement and nutraceutical products, polymeric carbohydrates, and other polymeric materials. The polymeric materials preferably comprise hydrophilic polymers in order to provide an effective oxygen-barrier. Accordingly, the matrix may comprise hydrocolloids. In addition, less water soluble polymers, i.e. hydrophobic polymers, may also be present in the matrix in order to provide some lipophilic character to the glassy matrix and thus to provide protection against moisture. In addition, the matrix may contain further components that are not polymeric, but that may assist in the formation of a dense glassy matrix or that may be added for other purposes.

Suitable proteins include caseins, whey proteins, soy protein, pectin and/or gelatine, for example. These proteins have good emulsification and film forming properties and can thus form the basis for polymer matrices.

The matrix component may comprise carbohydrates.

For example the matrix component may comprise monosaccharides, disaccharides, trisaccharides, oligosaccharides, polysaccharides or mixtures thereof.

Suitable monosaccharides include D-Apiose, L-Arabinose, 2-Deoxy-D-ribose, D-Lyxose, 2-O-Methyl-D-xylose, D-Ribose, D-Xylose, which are all Pentoses or Hexoses like for instance L-Fucose , L-galactose, D-Galactose, D-Glucose, D-Mannose, L-Rhamnose, L-mannose, or mixtures of several of these.

Mono- and dissacharides may be reduced to the corresponding alcohols, for example xylitol, sorbitol, D-mannitol and/or maltitol. Similarly, oxidation to aldonic, dicaroxyclic acids or uronic acids and reactions with acids, alkalis or amino compounds can give rise to many other compounds like isomaltol, for instance, which may be comprised in the matrix component of the present invention.

Suitable oligosaccharides are molecules consisting of from 3–10 monosaccharide units, such as maltopentaose, fructo- and/or galactooligosaccharides.

Polysaccharides, that is, saccharides containing more than 10 monosaccharide units per molecule are particularly preferred. These polymers can be either perfectly linear (cellulose, amylose), branched (amylopectin, glycogen) or linearly branched. They can include carboxyl groups (pectin, alginate, carboxymethyl cellulose) or strongly acidic

groups (furcellaran, carrageenan or modified starch). They can be modified chemically by derivatization with neutral substituents (in the case of methyl ethyl cellulose or hydroxypropyl cellulose for instance) or acidic substituents (with carboxymethyl, sulphate or phosphate groups).

The matrix component may comprise gums and/or hydrocolloids, for example, gum Arabic, agar agar and the like.

Preferably, the matrix component comprises a starch and/or a starch derivative such as pre-gelatinised starch, thin- or thick-boiling starch, dextrins or maltodextrins of various molecular weights. Most preferably, the matrix component comprises maltodextrin and/or corn starch syrup having a mean dextrose equivalence of 5–25, preferably 6-20, more preferably 10-18. Other possible modifications of starch and resulting derivatives suitable as a matrix component include octenyl-succinated starch, starch ethers (e.g. carboxymethyl starch), starch esters (e.g. starch monophosphate), cross-linked starch and/or oxidised starch.

In a preferred embodiment, the matrix component comprises, per dry weight of the glassy matrix alone, 60-95 wt % of maltodextrin, preferably with a DE value in the above indicated ranges, and 5-40 wt % of modified starch, such as alkenyl-succinated starch, (in particular octenyl-succinated starch).

While the above matrix-materials are preferred in case of applications of the capsules to food products and/or beverages, there may be numerous further materials suitable when the capsules are not intended for addition to food products. For example, in capsules comprising fragrance or malodour control ingredients, the matrix material may be selected from a much wider range of materials. These include synthetic polymers, co-polymers or natural non-food polymers, salts and other fillers may be used as matrix materials. These include cellulose and/or hemi-cellulose, as well as cellulose derivatives.

The matrix component may comprise mixtures of the above- and/or below mentioned carbohydrates, their derivatives and/or proteins. For example, mono-di or trisaccharides and/or their reaction products (see above) may be used as additives in combination with a protein or polysaccharide based matrix and thus bring properties as desired to the matrix component.

The feed prepared in a step of the present method preferably comprises 10-70 wt % of matrix materials, 30-70 wt % of water and 5-35 wt % of active ingredient. More preferably, the percentages are in the range of 20-40, 40-60 and 10-30 wt %, and

most preferably 25-35, 45-55 and 15-20 wt % of matrix materials, water and active ingredient, respectively, in the spray drying feed.

According to a preferred embodiment of the process of the present invention, the feed comprising the active ingredient, matrix components and water has a dry matter content in the range of 45-80 wt %, preferably 50-70 wt %. The relatively high dry-matter content entails a high viscosity emulsion, rather difficult to handle and guide into the spraying tower. On the other hand, thanks to a high dry-matter content, the drying process becomes more efficient as less water needs to be evaporated. Unlike in conventional spray drying, where the feed's droplet diameter size is less than 150 µm, the present invention enables a successful drying of comparatively larger drops. Feed of higher viscosity can be dried because it is not necessary to create a fine spray, the use of the powdering agent making it possible to dry very large drops.

The present invention comprises a step of introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower. Such powdering agents are mainly intended to provide a coating of powdering agent on the drops of the sprayed feed. According to the invention, this powdering agent may comprise, in addition to the coating or anti-caking component, a component capable of reacting with the material or materials of the encapsulating matrix to modify the dissolution properties of the capsules in aqueous media.

The "coating or anti-caking component" forming part or the whole of the powdering agent according to the invention is intended to mean here any ingredient that is capable of sticking to the wet feed droplet and absorb water to a certain degree. Such agents are preferably selected from the group consisting of starch, starch derivatives, talc, bentonite, silicon dioxide, calcium, magnesium, aluminium or potassium silicates, sodium, potassium or calcium aluminosilicates, calcium, sodium or magnesium carbonates, calcium or magnesium phosphates, ferric ammonium citrate, microcrystalline cellulose and cellulose derivatives or fibres, aluminium, calcium, sodium, magnesium, potassium or ammonium salts of fatty acids, magnesium oxides and mixtures comprising two or more of the aforementioned powdering agents. The purpose of this coating or anti-caking component is to prevent the dispersed feed drops from attaching to each other and/or to the inner walls of the spraying tower. It may be present in a proportion of 0.1 to 30% by weight of the feed's total solids weight.

The "reacting component or reactant" agent, possibly a part of the powdering agent, is intended to mean here any compound or substance that is capable of reacting with the carrier or matrix materials of the feed being sprayed in order to induce gelling, polymerisation, cross linking, crystallization or any other chemical or physical transformation of said matrix material susceptible of modifying its water dissolution properties. Thus the nature of the reacting component depends on the nature of the matrix material used in the feed of active ingredient and can therefore be selected by the person skilled in the art accordingly.

For inducing the modification of the dissolution properties of the matrix, it is essential to have a reactant in the feed that can react with at least one of the feed's components, either during the spraying of the feed or at a later stage when the solid capsules are incorporated into an end product where this reaction becomes possible. Thus at least two components must be present in the spraying tower, one gelling agent, monomer or polymer in the feed and a reactant, preferably a solid material, capable of reacting with the gelling agent, monomer or polymer of the feed to modify the water solubility of the final matrix encapsulating the active ingredient in the obtained granules.

According to particular embodiments of the invention the reactant or reacting component is part of the powdering agent and is a solid material admixed with the coating or anti-caking component, both being fed through the same inlet into the spraying tower as the feed is being sprayed. The particles of the feed will thus be coated with the anti-caking agent whilst their matrix undergoes the modifying reaction capable of changing its water dissolution properties.

The powdering agent is thus suspended in the tower and creates a coating on the dispersed drops as soon as they enter the tower. Accordingly, in a preferred embodiment of the invention, particles of the powdering agent are suspended in the spraying tower and circulate from an inlet into the spraying tower to an outlet, which outlet is also the outlet of the hot gas.

Generally, the powdering agent itself moves in circuit from an inlet for the powdering agent into the drying tower, to an outlet where it exits together with exhaust gas. The powdering agent may be recycled in a cyclone collector from which it may be redirected by a powdering agent return pipe to the inlet into the spraying tower. Preferably, the powdering agent circulates, at least partly, in counter current with the dispersed drops of the feed. Accordingly, in a preferred embodiment of the invention,

spare powdering agent not absorbed on the dispersed capsules exits the spraying tower together with the hot gas through an outlet of exhaust gas, which leads to a cyclone or a filter bag house separating the hot gas from the powdering agent, and whereby the powdering agent is reintroduced into the spraying tower thus forming a continuous circulation of powdering agent from the cyclone to the spraying tower and back to the cyclone.

The dry anti-caking agent together with the dry reactant forming preferred powdering agents according to the invention will stick onto the wet surface of the large droplets of the feed. The reaction between the reactant and the matrix material can either start directly during the flight of the droplets or be induced by the release of the reactant in application, when the capsules are re-hydrated and/or when they are introduced in a medium in which the pH and/or temperature conditions, for instance, induce the release of the reactant.

The layer of anti-caking agent and possibly the reactant itself will prevent the large droplets from sticking onto the wall of the spraying chamber.

Both the anti-caking and reactant ingredients are preferably formed of powder particles of a diameter size below 100 μm and more preferably 50 μm.

The materials for the reactant or reacting component present in the powdering agent and/or in the feed must be adapted to the nature of the matrix material.

It goes without saying that this reactant may also be introduced in the spraying tower separately from the anti-caking component of the powdering agent. They must however be present simultaneously with the spraying of the feed. Moreover, the reactant may be sprayed in liquid form into the chamber via a second nozzle instead of being mixed dry with the anti-caking component of the powdering agent.

Several polymers/ monomers, gelling agent and/or several reactants can be used.

The reactant can also be introduced in the matrix formula together with the encapsulating polymer, provided that the pH conditions of the feed prevent the reactant from reacting with the polymer. An additional third substance may thus be needed in the tower to modify the spraying medium and thus trigger the reaction between the reactant and the polymer. For example, an insoluble form of a calcium salt may be incorporated in the matrix together with an alginate and the reaction between alginate and calcium triggered by a change in pH induced by the presence of an acid in the end application consumer product or at the surface of the granule upon contact of the latter with water.

The aqueous medium of the feed may contain organic solvents or alternatively the feed medium may be based on such solvents.

The process of the invention may be carried out in any spraying equipment, including any standard type spraying or drop producing device like rotary atomizers, high pressure nozzles, vibrating nozzles etc, a spraying chamber or tower, and a fluidised bed integrated at the bottom of the chamber or separate from it.

Optionally, an additional dryer can be used, similar to those known in the dairy industry equipments used in the 3-stage drying of instant powders.

Dosing units for the continuous introduction of the required amounts of anti-caking agent and reactant may also be provided in the equipment or apparatus of the invention.

The feed must be composed of at least a polymer or film-forming substance or any other ingredient capable of forming an encapsulating matrix to carry the active ingredient. The selection of this polymer may determine the nature of the reactant forming part of the spraying atmosphere and preferably incorporated in the powdering agent or alternatively, if an encapsulating polymer is inadequate to react with a particular reactant, a second matrix material may be added, namely a second polymer, gelling agent or monomer capable of reacting with the reactant to modify the matrix properties and dissolution properties in an aqueous medium and hence the kinetics of release of the active ingredient.

The process of the invention may be a spray drying or spray cooling process.

The so-called spray cooling differs from standard spray drying in the sense that the feed already contains a gelling agent or a compound having a melting point and capable of hardening the encapsulating matrix on cooling.

The same constraints as those of current spray drying processes are associated with spray cooling since the feed must also have a low viscosity and only fine droplets of less than 300 microns diameter can be properly solidified on cooling. The feed is always sticky so that the geometry of the current spraying chambers must be very large to permit a proper cooling of such large particles.

According to the invention, the spray cooling process involves the spraying of a feed comprising a matrix or carrier material capable of hardening on cooling either by gelling, crystallizing or solidifying. The feed is atomized in large droplets and comes into

contact in the tower with the dry powdering agent containing the reactant capable of modifying the dissolution properties of this matrix.

Both spray drying and spray cooling processes of the invention present the advantage of permitting the use of very sticky feed formulations, whereas in standard spraying processes the feed formula must be adapted to avoid the product to stick everywhere in the spraying chamber. Thus, standard feed formula could not contain large amounts of sugars or plasticizers for instance. The present invention solves this problem since the feed can contain raw materials that are difficult to handle by standard spray drying or spray cooling techniques.

The formed granules are collected in a fluidised bed at the bottom of the chamber where the chemical or physical reaction can eventually continue further until complete drying or hardening of the granules is achieved.

The inlet temperature of the air in the spraying tower may vary in a wide range of values, comprised between –20°C and +500°C. The process can be carried out either using a hot gas in order to dry the particles at least partially during their flight, or a cold gas to induce the hardening of the droplets, depending on the nature of the feed. As previously mentioned, particular embodiments of the process relate to inlet temperatures above 120°C.

In the case of a high inlet temperature (e.g. 150°C) a partial drying of the granules takes place in flight and the drying continues in the fluidized bed until the granules have reached the required final residual moisture.

In the case of low inlet temperatures (e.g. 5°C), the feed must either contain a gelling agent capable of hardening the matrix on cooling, or the chemical reaction between the feed and the reactant must be fast enough to sufficiently harden the droplets and adequately collect them in the fluidized bed. The granules are then dried or further hardened in a second phase of the process where the temperature of the fluidized bed is increased or in a separated part of the equipment (additional external fluid bed dryer/cooler for instance).

As previously mentioned, there is supplied into the spraying tower a hot gas having a temperature in the range of 121-250°C. In such embodiments of the invention the hot gas is supplied at a higher temperature than those disclosed in the prior art. It has been, surprisingly established that relatively large-sized drops comprising the active ingredient are preferably dried under supply of a gas having a higher temperature while

having less loss during drying. Without wishing to be bound by theory it is hypothesized that the higher temperature in the spraying zone brought about by the higher temperature of the inlet gas stream results in a shorter drying time. According to the invention, more water is evaporated from the drop during its flight, and the subsequent drying time in the fluidised bed is also shorter.

According to even more preferred embodiments, the hot gas supplied into the drying tower has a temperature in the range of 130-220°C, preferably 140-210°C, and most preferably 150-190°C.

The supply of hot gas through a hot gas inlet results in a temperature in the spraying tower in the range of about 180 to about 50°C, preferably about 170°C to about 40°C. The temperature in the tower follows a gradient, with the highest temperature at the hot gas inlet, which thus provides a high temperature at the spraying zone. At the bottom of the tower the temperature is much lower, due to the evaporation of water from the dispersed drops.

The method of the invention comprises the step of removing capsules comprising a coating of powdering agent from the spraying tower.

The process can be performed in batch or continuous mode. Accordingly, in batch mode, there will be provided an outlet at the level of the fluidised bed leading to a collecting vessel. By turning off the fluidised bed and opening the valve leading to the collecting vessel, the capsules are guided, for example by gravity, to the collecting vessel, from where they may be removed. In a preferred embodiment, the method of the invention is performed continuously, for example by conveying the granules from the integrated fluidised bed to an external, additional fluidised bed where the capsules may be further dried to accurately control their final moisture content. In the continuous mode, the residence time of the capsules in the whole process is reduced which is found to be beneficial to the quality of the product.

Preferably, the fluidised bed is supplied with a gas having a temperature in the range of 20°C to about 100°C, meaning that gas having a temperature in this range is supplied from below the bed through small apertures to fluidise/intercept the capsules. Preferably, the temperature of the gas is in the range of 65 to 90°C. Generally, the gas is air. Similarly to the spraying zone, the method of the present invention again provides for comparatively high temperatures in the fluidised bed in view of the prior art. Again a shorter drying period results in surprisingly lower loss of volatile ingredients.

The capsules obtainable and/or obtained by the method of the present invention may have an active ingredient load, e.g. a flavour and/or fragrance load, of 1–50 wt %. According to a preferred embodiment, the load of the active ingredient is in the range of 18–50 wt %. It is thus possible to have high active ingredient loads in the range of 20–40 wt %, preferably 25–38 wt % and more preferably 27 to 35 wt %.

Higher ingredient loads are obtainable by the processes of the present invention wherein comparatively high temperatures of the inlet gas are used, thus resulting in distinctly superior volatile ingredient loads being obtained than when prior known methods are used. The high loads are further a consequence of reduced loss of volatiles achieved by the present method.

Generally, the contribution of the powdering agent to the total weight of the capsules may be in the range of 0.1 to 30%, which corresponds to a preferred embodiment of the present invention. However, the present invention allows for the reduction of the amount of powdering agent to 0.1 to 27 wt %, preferably 0.5 to 25 wt %, more preferably 1 to 20 wt % and most preferably 2–15 wt % of powdering agent. In a preferred embodiment, the amount of powdering agent makes up $\leq$ 10 wt % of the total weight of the capsules of the present invention.

The present invention further provides capsules obtainable and/or obtained by the method of the present invention.

The present invention also provides a food product comprising the capsules of the invention and/or the capsules obtainable by the method of the invention. Products may be, for example, food products in which the active ingredient of the capsules is a flavour ingredient.

The invention also encompasses perfumed products comprising the capsules of the invention, in which the active ingredient is a perfuming composition, for example a perfume, an eau-de-toilette, or another composition of perfuming ingredients optionally further comprising solvents and/or other adjuvants.

The encapsulation of active pharmaceutical ingredients is also encompassed by the present invention which thus also relates to medicinal formulations and pharmaceutical products containing them.

The application of the capsules obtainable by the process of the invention is most useful and advantageous whenever controlled release of active ingredients is desired upon use in an aqueous or moisture containing environment. The preparation of powders for

instant drinks for example will especially benefit from these capsules as will instant soup preparations, taste-masking applications, chewing gums, low fat food or other food applications. These capsules may also find applications in the pharmaceutical or cosmetic industry, when controlled release of an active is desired.

The invention will now be illustrated by way of the following examples.

Examples

In the following examples the following general conditions were applied: a small scale spray drier/cooler of the Niro® FSD0.8 type, with integrated fluidized bed was used to carry out the processes; in this spray drier, the main air stream was introduced in an annular space around the atomizing nozzle on top of the spraying chamber and also exhausted also from the ceiling of the same chamber; the exhaust air passed through a cyclone where the fine particles, including the anti-caking agent and the reactant, were collected and returned into the chamber using an additional air stream; a fluidized bed was integrated at the bottom of the chamber to collect the wet granules surrounded by the anti-caking agent and reactant. A third air stream passed through the perforated plate in the fluidized bed in order to dry the granules.

Example 1

Preparation of capsules containing limonene

a) Preparation of the dry anti-caking agent and reactant mixture forming the powdering agent

250 G of native Starch type B from Roquette Frères SA were mixed with 150 g of dry Calcium Gluconate (Fluka) using a mechanical blender (HUG Maschinenbau, Switzerland). 0.4 G of fumed silica, Aerosil® 200 from Degussa were added to increase the flowability of the powder mixture.

b) Preparation of the feed

65.5 G of modified starch (Capsul®, National Starch), 5 g of citric acid and 50 g sucrose were dissolved together into 1150 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained. 29.5 G of alginate (protanal LF10/60 from FMC

Biopolymer) was then added until complete dissolution. 150 G of pure limonene were emulsified into the modified starch solution using an UltraTurrax® UT25 rotor/stator high shear mixer rotating at 23000 rpm for 2 minutes.

c) Processing conditions

- Inlet main air stream temperature = 100°C
- Inlet main air stream flow rate = 55 Kg/h
- Fluidized bed air stream temperature = 65°C
- Fluidized bed air stream flow rate = 24 Kg/h
- Fine return air stream temperature = 50°C
- Fine return air stream flow rate = 11 Kg/h
- Nozzle gas flow rate = 3 Kg/h
- Diameter of the nozzle = 1mm
- Feed temperature = 40°C

At the beginning of the process the powdering agent mixture (i.e. the native starch and Calcium gluconate blend) was introduced in the chamber via a hole in the ceiling. This powder mixture was thus immediately fluidized into the chamber and recycled in closed loop continuously.

After all the temperature settings had reached the desired values in the apparatus, the feed was atomized during 10 minutes at a feed flow rate of 0.055 l/min.

The atomization was then stopped and the granules were kept fluidized into the fluidized bed during 15 more minutes.

180 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. Their average diameter was of 350 microns. Figure 1 shows the general aspect of the obtained dry granules.

In order to check that the granules were insoluble in water, 1 g of these granules were introduced into 500 ml of cold water. After hydration white granules were clearly visible and the water phase remained clear, as is shown in Figure 2. The limonene emulsion droplets were trapped into an alginate gel and couldn't migrate into the water phase.

Example 2

Preparation of capsules containing limonene

a) Preparation of the dry anti-caking agent and reactant

200 G of native Starch type B from Roquette Frères SA were mixed with 100 g of dry Calcium Gluconate (Aldrich 22,764-1) using a mechanical blender (HUG Maschinenbau, Switzerland).

b) Preparation of the feed

100 G of modified starch (Capsul®, National Starch), 640 g of maltodextrin 10-18DE and 60 g of pectin (Unipectine OF 305 from Degussa) were dissolved together into 1100 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained.
200 G of pure limonene were emulsified into the modified starch solution using an UltraTurrax® UT25 rotor/stator high shear mixer rotating at 23000 rpm for 2 minutes.

c) Processing conditions

- Inlet main air stream temperature = 210°C
- Inlet main air stream flow rate = 75 Kg/h
- Fluidized bed air stream temperature = 75°C
- Fluidized bed air stream flow rate = 24 Kg/h
- Fine return air stream temperature = 50°C
- Fine return air stream flow rate = 11 Kg/h
- Nozzle gas flow rate = 20 nl/min
- Diameter of the nozzle = 1mm
- Feed temperature = 40°C

At the beginning of the process the powder mixture was introduced into the chamber via a hopper connected to the fine return pipe. This powder mixture was thus immediately fluidized into the chamber and recycled in closed loop continuously.
After all the temperature settings were obtained in the equipment, the feed was atomized during 10 minutes at a feed flow rate of 0.057 l/min.

The atomization was then stopped and the granules were kept fluidized into the fluidized bed during 10 more minutes.

270 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. Their average diameter was of 500 microns.

In order to check that the granules were insoluble in water, 1 g of these granules were introduced into 1000 ml of warm water (60°C). After hydration white granules were clearly visible and the water phase remained clear. The limonene emulsion droplets were trapped into a pectin gel and couldn't migrate into the water phase.

The final limonene load was of 15% w/w based on the final weight of the granules. The granule contained on their surface about 20% w/w of a mixture of dry Ca-gluconate and native starch. The loss of flavour compared to the amount contained in the original feed was less than 10%, showing that the process is very effective for the encapsulation of such highly volatile active ingredients. Note that the final amount of Ca-gluconate and native starch present at the surface of the granules has to be taken into consideration for the calculation of the flavour losses.

Example 3

Preparation of capsules containing limonene

The same processing conditions as those of Example 2 were used, except that the formulation contained a lesser amount of pectin.

Preparation of the feed:

100 G of modified starch (Capsul®, National Starch), 680 g of maltodextrin 10-18DE and 20 g of pectin (Unipectine OF 305 from Degussa) were dissolved together into 1100 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained.

200 G of pure limonene were emulsified into the modified starch solution using a rotor/stator high shear mixer UltraTurrax® UT25 rotating at 23000 rpm for 2 minutes.

270 G of dry granules were collected in a glass vessel.

The final limonene load was also of 15% w/w based on the final weight of granules.

Although the amount of pectin was much lower, the particles still jellified in warm water and the limonene droplets were trapped in a gelled matrix.

Examples 4 and 5

Preparation of flavour-containing capsules

Two flavours, a minty tonality flavour (880335 NF from Firmenich SA), respectively a strawberry tonality flavour (502301 TA from Firmenich SA), were encapsulated in identical conditions to those described in Example 3 to provide flavoured capsules of flavour active material and which behaved similarly when introduced in warm water. The final flavour load was 33.3 weight % for the minty flavoured capsules, respectively 35.2 weight % for the strawberry flavoured capsules, in both cases the particles having an average diameter of 350 micron.

Example 6

Preparation of capsules containing perfume

a) Preparation of the dry anti-caking agent and reactant mixture forming the powdering agent

225 G of native Starch type B from Roquette Frères SA were mixed with 75 g of dry DiSodium Sulfate (Na_2SO_4 - Fluka) using a mechanical blender (HUG Maschinenbau, Switzerland).

b) Preparation of the feed

207.6 g of Polyvinyl Alcohol (Erkol V03/1410), 28 g of Sucrose and 0.4 g of antifoam, were dissolved together into 800 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained. 164 g of Perfume (Loving UN 147988) were emulsified into the Polyvinyl Alcohol/sucrose solution using an UltraTurrax® UT25 rotor/stator high shear mixer rotating at 23000 rpm for 2 minutes.

c) Processing conditions

- Inlet main air stream temperature = 230°C
- Inlet main air stream flow rate = 75 Kg/h
- Fluidized bed air stream temperature = 75°C
- Fluidized bed air stream flow rate = 23 Kg/h

- Fine return air stream temperature = 50°C
- Fine return air stream flow rate = 16 Kg/h
- Nozzle gas flow rate = 3 Kg/h
- Diameter of the nozzle = 1mm
- Feed temperature = 40°C

At the beginning of the process the powdering agent mixture was introduced in the chamber via a hopper connected to the fine return line. This powder mixture was thus immediately fluidized into the chamber and recycled in closed loop continuously.

After all the temperature settings had reached the desired values in the apparatus, the feed was atomized during 10 minutes at a feed flow rate of 0.055 l/min.

The atomization was then stopped and the granules were kept fluidized into the fluidized bed during 15 more minutes.

180 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. Their average diameter was of 350 microns.

In order to check that the granules were insoluble in water, 1 g of these granules were introduced into 500 ml of cold water. After hydration white granules were clearly visible and the water phase remained clear, as is shown in Figure 2. The perfume emulsion droplets were trapped into a Polyvinyl alcohol matrix which dissolved very slowly since Polyvinyl Alcohol precipitate in presence of the Disodium Sulfate.

Example 7

Preparation of capsules containing limonene by internal gelation

a) Preparation of the dry anti-caking agent and reactant mixture forming the powdering agent

250 G of native Starch type B from Roquette Frères SA were mixed with 150 g of dry Citric acid using a mechanical blender (HUG Maschinenbau, Switzerland). 0.4 G of fumed silica, Acrosil® 200 from Degussa were added to increase the flowability of the powder mixture.

b) Preparation of the feed

60.5 G of modified starch (Capsul®, National Starch) and 50 g sucrose were dissolved together into 1150 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained. 10 G of Dicalcium Phosphate (Fluka) were added to the solution and a suspension of Dicalcium phosphate in the modified starch/sucrose solution was created. 29.5 G of alginate (protanal LF10/60 from FMC Biopolymer) was then added until complete dissolution. 150 G of pure limonene were emulsified into the suspension of Dicalcium Phosphate solution using an UltraTurrax® UT25 rotor/stator high shear mixer rotating at 23000 rpm for 2 minutes.

c) Processing conditions

- Inlet main air stream temperature – 100°C
- Inlet main air stream flow rate = 55 Kg/h
- Fluidized bed air stream temperature = 65°C
- Fluidized bed air stream flow rate = 24 Kg/h
- Fine return air stream temperature = 50°C
- Fine return air stream flow rate = 11 Kg/h
- Nozzle gas flow rate = 3 Kg/h
- Diameter of the nozzle = 1mm
- Feed temperature = 40°C

At the beginning of the process the powdering agent mixture (i.e. the native starch and citric acid blend) was introduced in the chamber via a hole in the ceiling. This powder mixture was thus immediately fluidized into the chamber and recycled in closed loop continuously.

After all the temperature settings had reached the desired values in the apparatus, the feed was atomized during 10 minutes at a feed flow rate of 0.055 l/min.

The atomization was then stopped and the granules were kept fluidized into the fluidized bed during 15 more minutes.

180 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. Their average diameter was of 350 microns. Figure 1 shows the general aspect of the obtained dry granules.

In order to check that the granules were insoluble in water, 1 g of these granules were introduced into 500 ml of cold water. After hydration white granules were clearly visible

and the water phase remained clear. The limonene emulsion droplets were trapped into an alginate gel and couldn't migrate into the water phase.

The Dicalcium Phosphate is an insoluble calcium salt at neutral pH. A gel of alginate was thus formed into the matrix when the citric acid present at the surface of the granules was dissolved in water. The local pH around the granules was decreased and calcium ions were released by the dissolution of Dicalcium Phosphate at such low pH. This principle is called internal gelation of alginate.

Example 8

Preparation of capsules containing a sweetener

a) Preparation of the dry anti-caking agent and reactant

200 G of native Starch type B (Roquette Frères SA) were mixed with 100 g of dry Calcium Gluconate (Aldrich 22,764-1) using a mechanical blender (HUG Maschinenbau, Switzerland).

b) Preparation of the feed

100 G of modified starch (Capsul®, National Starch), 660 g of maltodextrine 10-18DE and 40 g of pectin (Unipectine OF 305 from Degussa) were dissolved together into 1100 g of warm water (50°C) using a dissolver disk until a clear yellow solution was obtained. 200 G of aspartame were added to the modified starch solution using an UltraTurrax® UT25 rotor/stator high shear mixer rotating at 23000 rpm for 2 minutes.

c) Processing conditions

- Inlet main air stream temperature = 210°C
- Inlet main air stream flow rate = 75 Kg/h
- Fluidized bed air stream temperature = 75°C
- Fluidized bed air stream flow rate = 24 Kg/h
- Fine return air stream temperature = 50°C
- Fine return air stream flow rate = 11 Kg/h
- Nozzle gas flow rate = 25 nl/min
- Diameter of the nozzle = 1mm
- Feed temperature = 40°C

At the beginning of the process the powder mixture was introduced into the chamber via a hopper connected to the fine return pipe. This powder mixture was thus immediately fluidized into the chamber and recycled in closed loop continuously.

After all the temperature settings were obtained in the equipment, the feed was atomized during 10 minutes at a feed flow rate of 0.057 l/min.

The atomization was then stopped and the granules were kept fluidized into the fluidized bed during 10 more minutes.

75 G of dry granules were collected in a glass vessel connected to the fluidized bed via a butterfly valve. The average diameter was 58g >210 microns and 17 g >500 microns.

In order to check that the granules were insoluble in water, 1 g of these granules was introduced into 1000 ml of warm water (60°C). After hydration white granules were clearly visible indicating delayed solubility in water.

The final aspartame load was of about 16 % w/w based on the final weight of the granules. The granule contained on their surface about 20% w/w of a mixture of dry Ca-gluconate and native starch.

Claims

1. A process for preparing capsules having an average diameter in the range of 100 to 2000 µm and comprising an active ingredient, the process comprising the steps of

a) preparing a solution, suspension and/or emulsion comprising the active ingredient, a carrier or matrix material and a solvent to form a feed;

b) spraying the feed in the form of drops having a mean diameter of 100 to 2000 µm into a spraying tower,

c) introducing, simultaneously to the spraying-step, a powdering agent into the spraying tower;

d) supplying, simultaneously to the spraying step, a gas having a temperature in the range of –20°C to 500°C into the spraying tower; and,

e) removing the capsules from the spraying tower;

wherein, simultaneously with the addition of the powdering agent used in step c), there is introduced into the spraying tower a reactant capable of reacting with said carrier material to modify the dissolution properties of the obtained capsules into aqueous media.

2. A process according to claim 1, wherein a hot gas is supplied into the spraying tower, at a temperature of 50°C to 500°C in step d) of the process.

3. A process according to claim 2, wherein the temperature of the hot gas is in the range of 100°C to 250°C, more preferably in the range of 120°C to 200°C.

4. A process according to claim 1, wherein the temperature of the gas is below 30°C, more preferably between –20°C and 10°C.

5. The process of claim 2, further comprising the step of intercepting the capsules by a fluidised bed after being coated by the powdering agent and after being at least superficially dried by the hot gas in the spraying tower.

6. A process of any one of the preceding claims, wherein the solvent is water-based.

7. The process of claim 1 or 6, wherein the powdering agent comprises the reactant capable of reacting with the carrier material of the feed.

8. The process of claim 5, in which the fluidised bed is supplied with a gas having a temperature in the range of 41 to about 100°C.

9. The process of claim 6, wherein the feed comprising the active ingredient has a dry matter content in the range of 10 to 80 wt %, preferably in the range 45 - 75 wt %.

10. The process of claim 1, wherein the capsules have a flavour and/or fragrance ingredient load of 0.1 - 70 wt %, preferably 10 - 50 wt %.

11. The process according to claim 1, wherein the matrix materials in the feed comprise polysaccharides, and, preferably saccharides selected from the group of mono- and/or disaccharides, trisaccharides and oligosahharides.

12. A process according to claim 1 or 7, wherein the powdering agent provides a coating on the surface of the capsules representing 0.1 to 30 wt % of the total weight of the capsules.

13. A process according to any of claims 1 to 12, wherein the carrier or matrix material is selected from the group consisting of dextrins, proteins, starch, modified starch, corn syrups, cellulose and derivatives thereof, gums, hydrocolloids, microbial polysaccharides, and mixtures of two or more of these materials.

14. A process according to claim 13, wherein the powdering agent is selected from the group consisting of starch, starch derivatives, talc, bentonite, silicon dioxide, calcium, magnesium, aluminium or potassium silicates, sodium, potassium or calcium aluminosilicates, calcium, sodium or magnesium carbonates, calcium or magnesium phosphates, ferric ammonium citrate, microcrystalline cellulose and cellulose derivatives or fibres, aluminium, calcium, sodium, magnesium, potassium or ammonium salts of fatty acids, magnesium oxides and mixtures comprising two or more of these materials.

15. A process according to claim 13 or 14, wherein the reactant is a substance capable of reacting with the carrier material to induce gelling, polymerization, cross linking, crystallization or any other chemical or physical transformation thereof susceptible of modifying said carrier material water dissolution properties.

16. A process according to any one of claims 13 to 15, wherein the carrier material comprises modified starch, possibly in admixture with maltodextrine and/or a protein, the powdering agent is native starch and the reactant is calcium gluconate.

17. A process according to any one of claims 13 to 15, wherein the carrier material comprises polyvinyl alcohol, the powdering agent is native starch and the reactant is disodium sulfate.

18. Capsules comprising an active ingredient, obtainable by the process according to any one of claims 1 to 17.

19. Capsules having an average diameter in the range of 100 to 2000 µm comprising an active ingredient, the load of active ingredient being in the range of 0.1 – 70 wt %, the capsules comprising a coating provided by a powdering agent, whereby the coating provides 0.1 to 30 wt % of the total weight of the capsules.

20. A method for controlling the water dissolution properties of sprayed particles containing an active ingredient and having an average diameter of from 100 to 2000 µm, wherein the particles are prepared according to the process of any one of claims 1 to 17.

21. A consumer product comprising the capsules according to claim 18.

22. A consumer product comprising the capsules according to claim 19.

23. A consumer product according to claim 21 or 22, in the form of a perfume, soap, cosmetic or other body care product, hair care product, food or beverage, chewing gum or oral care product such as a mouthwashes or toothpaste, a pharmaceutical or food supplement.

FIGURE 1

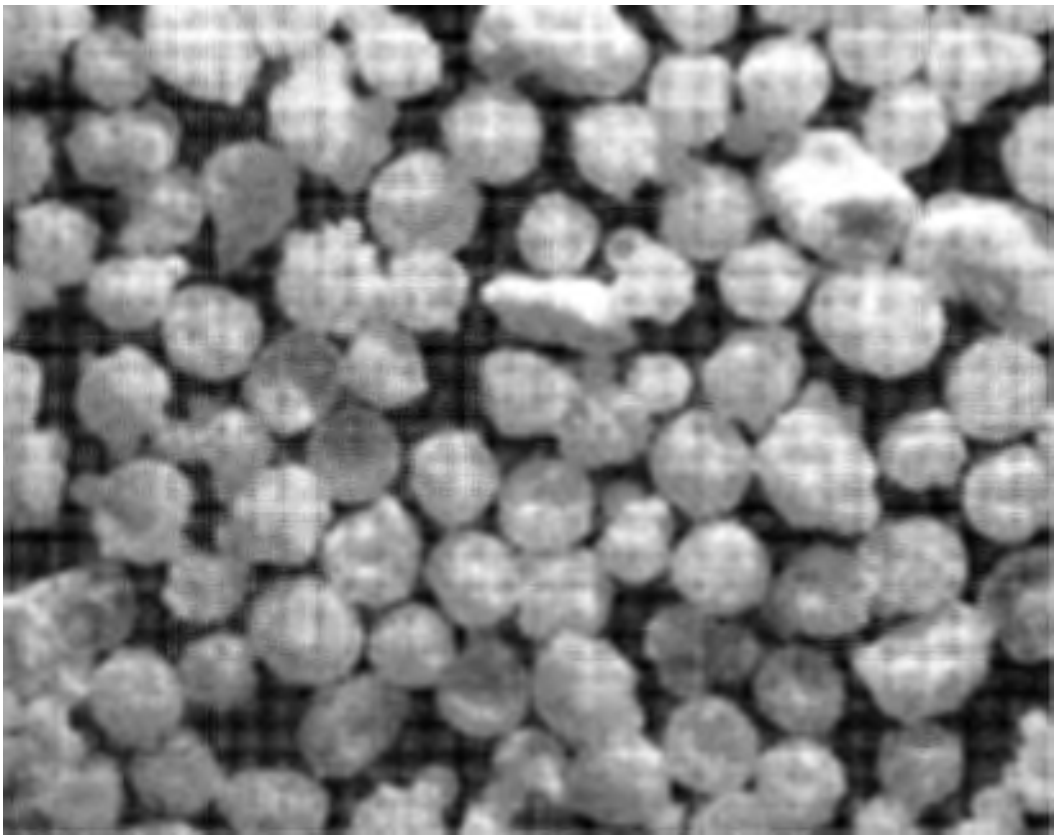
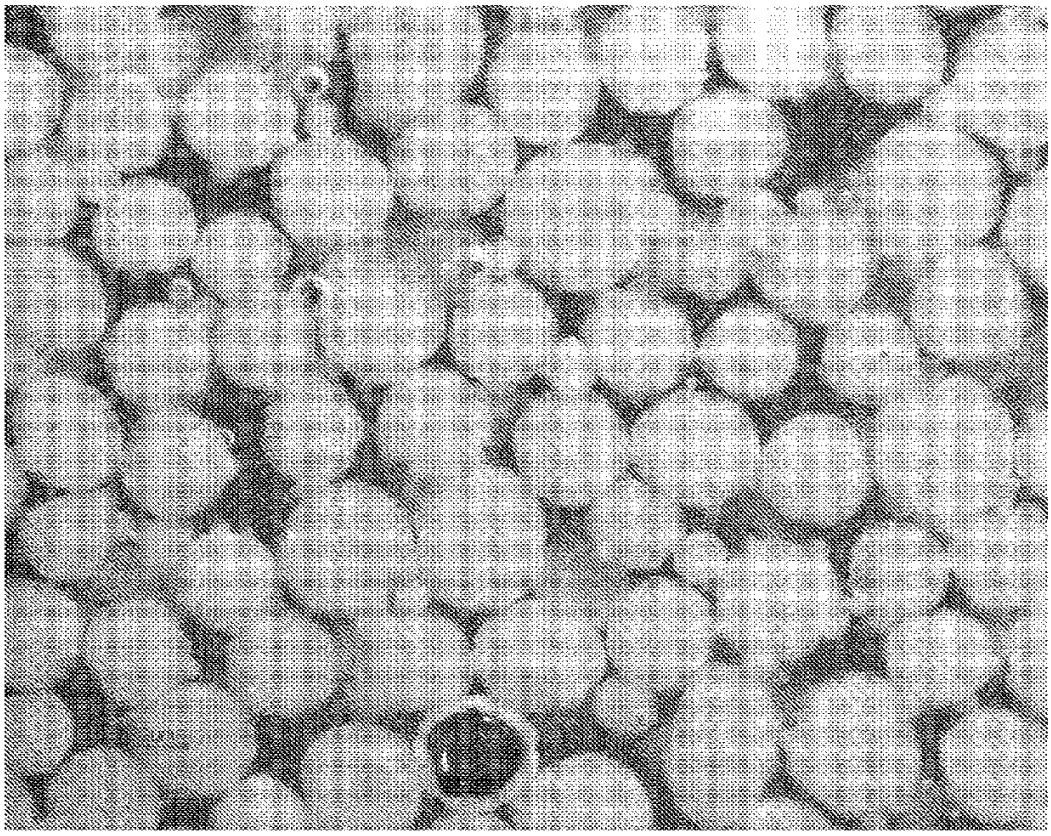


FIGURE 2



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(74) Agent: **DALE, Gavin**; Firmenich Sa, 1, route des Jeunes P. O. Box 239, CH-1211 Geneva 8 (CH).

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(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: ONE STEP SPRAY-DRYING PROCESS

(57) Abstract: Capsules encapsulating an active or functional ingredient are obtainable by a process in which a feed comprising this ingredient is dispersed in the form of drops in a spraying tower and exposed to a temperature in the range of -20°C to 500°C. In the tower, a cloud of suspended powdering agent provides a coating and prevents the capsules from sticking together and a reactant is provided to react with a polymer or film forming carrier of the active ingredient so as to modify the water solution properties of the capsule walls.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/051655

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/00 A23L1/22 A23P1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L A23P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 634 598 A (LIU RICHARD T [US] ET AL) 6 January 1987 (1987-01-06) claims; examples; tables 1,2	18-23
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X	FR 2 758 055 A (SEA OIL [FR]) 10 July 1998 (1998-07-10) claims	18-23

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Vernier, Frédéric

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JACKSON L S ET AL: "MICROENCAPSULATION AND THE FOOD INDUSTRY" FOOD SCIENCE AND TECHNOLOGY, ACADEMIC PRESS, US, vol. 24, 1991, pages 289-297, XP001009807 ISSN: 0023-6438 page 293, left-hand column, paragraph 2	1-23
A	SOOTTITANTAWAT A ET AL: "Influence of emulsion and powder size on the stability of encapsulated d-limonene by spray drying" INNOVATIVE FOOD SCIENCE AND EMERGING TECHNOLOGIES, ELSEVIER, AMSTERDAM, NL, vol. 6, no. 1, March 2005 (2005-03), pages 107-114, XP004914127 ISSN: 1466-8564 the whole document	1-23

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Information on patent family members

International application No
PCT/IB2007/051655

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(54) Title: A SPRAY-DRYING PROCESS FOR PREPARING A LOW DENSITY, LOW BUILDER, HIGHLY WATER-SOLUBLE SPRAY-DRIED DETERGENT POWDER

(57) Abstract: The present invention relates to a spray-drying process for the preparation of a spray- dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0wt% to 10wt% zeolite builder and from 0wt% to 10wt% phosphate builder, and wherein the process comprises the step of: (a) preparing an aqueous slurry suitable for spray-drying comprising from 30wt% to 60wt% water and from 40wt% to 70wt% non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component, wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3: 1 to 5: 1; and (b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65°C to 140°C, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70°C to 120°C.

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A SPRAY-DRYING PROCESS FOR PREPARING A LOW DENSITY, LOW BUILDER, HIGHLY WATER-SOLUBLE SPRAY-DRIED DETERGENT POWDER

FIELD OF THE INVENTION

The present invention relates to a spray-drying process for the preparation of a low density, low builder, highly water-soluble spray-dried powder. The spray-dried powder is suitable for use as a solid laundry detergent composition, or for incorporation into a solid laundry detergent composition. The spray-drying process comprises the step of spray-drying an aqueous slurry comprising a large amount of water. The conditions of the spray-drying process promote steam puffing; which in turn leads to the formation of spray-dried detergent powder having a very low bulk density. The spray-dried detergent powder exhibits excellent solubility upon contact with water, even in cold water temperatures, such as 20°C or lower.

BACKGROUND OF THE INVENTION

In recent years, the manufacturers of solid laundry detergent products have focused their efforts into formulating highly water-soluble laundry detergent compositions that exhibit a good cleaning performance and a good dissolution performance in water. Some examples of these efforts are described in: DE19912679 and WO03/038028, both by Henkel KGaA; EP1416039 and EP1416040, both by Dalli-Werke Wasche und Korperflege GmbH & Co.KG; and WO05/083046, WO05/083048, WO05/083049, WO06/020788, WO06/020789, WO06/088665, WO06/088666, EP1690921 and EP1690922, all by The Procter & Gamble Company.

These attempts typically remove a large proportion of the composition, namely the zeolite and/or phosphate builder, and preferably at least some sulphate salt. This in turn means that a lower dosage of the composition during the laundering process is required. However, many consumers do not want to dose a smaller volume of detergent during their laundering process. Therefore, there remains a need to significantly reduce the bulk density of these low builder laundry detergent compositions. This in turn enables the consumer to dose the same volume of these low builder laundry detergents they have used in the past for the more

conventional high builder laundry detergents, during their laundering process. The use of low builder laundry detergent powders, due to their improved solubility in water, enables lower washing temperatures to be used, which improves the environmental and economic cost of the laundering process.

SUMMARY OF THE INVENTION

The Inventors have overcome the above problem of by providing a spray-drying process according to claim 1.

DETAILED DESCRIPTION OF THE INVENTION

Spray-drying process. The spray-drying process comprises the steps of preparing an aqueous slurry, and spraying the aqueous slurry into a spray-drying tower.

Typically, the aqueous slurry is prepared at a temperature in the range of from 60°C to 80°C. Typically the liquid ingredients, including ingredients in the form of a hot-melt, such as chelants, polymeric carboxylates, linear alkyl benzene sulphonate, that make up the aqueous slurry, including the water, are pre-heated to a temperature in the range of from 60°C to 80°C.

Preferably, essentially all of the detersive surfactant, if present, is contacted to the water before essentially any polymer is contacted to the water. Preferably essentially all of the polymer, if present, is contacted to the water before essentially any inorganic material. This is especially preferred as it ensures the optimal phase chemistry of the aqueous slurry for spray-drying.

Typically, the temperature of the aqueous slurry as it enters the spray-drying tower is in the range of from 50°C to 140°C, preferably from 60°C, or from 70°C, and preferably to 120°C, or to 99°C or to 95°C or to 90°C, or to 85°C, or even to 80°C.

Typically, the outlet air temperature of the spray-drying tower is in the range of from 50°C to 200°C, preferably from 60°C, or from 70°C or even 80°C, and preferably to 140°C, or to 120oC, or to 99oC or to 95°C or to 90°C, or even to 85°C.

Typically, the air flow rate in the spray-drying tower is in the range of from $1m^3s^{-1}$ to $40m^3s^{-1}$, preferably from $5m^3s^{-1}$, or from $10m^3s^{-1}$ or from $15m^3s^{-1}$ or even from $20m^3s^{-1}$, and preferably to $35m^3s^{-1}$, or even to $30m^3s^{-1}$.

Typically, the maximum cross-sectional area of the spray-drying tower is in the range of from $2m^2$ to $70m^2$, preferably from $10m^2$, or from $20m^2$, or from $30m^2$, or from $40m^2$, and preferably to $60m^2$.

Typically, the ratio of (i) the air flow rate in the spray-drying tower to (ii) the maximum cross-sectional area of the spray-drying tower is in the range of from $0.15ms^{-1}$ to $4ms^{-1}$, preferably from $0.2ms^{-1}$, or from $0.3ms^{-1}$, or even from $0.4ms^{-1}$, and preferably to $3ms^{-1}$, or to $2ms^{-1}$, or to $1ms^{-1}$, or even to $0.75ms^{-1}$. This is especially preferred in order to control the residency time of the aqueous slurry in the spray-drying tower so as to ensure adequate drying time. This is even more preferred when it is desirable to spray-dry at lower air temperatures.

Typically, the aqueous slurry is sprayed into the spray-drying tower through at least one nozzle, preferably multiple nozzles, having an aperture in the range of from 2mm to 5mm, preferably from 3mm, or from 3.5mm, and preferably to 4mm.

Typically, the slurry is sprayed into the spray-drying tower at a pressure in the range of from $4.0 \times 10^6 Nm^{-2}$ to $9.0 \times 10^6 Nm^{-2}$, preferably from $5.0 \times 10^6 Nm^{-2}$, and preferably to $7.0 \times 10^6 Nm^{-2}$, or even to $6.0 \times 10^6 Nm^{-2}$. These pressures, especially these low pressures, promote steam puffing, which in turn lead to the formation of spray-dried detergent powder having a very low density.

Typically, the ratio of (i) the rate in gs^{-1} units at which the aqueous slurry is sprayed into the spray-drying tower to (ii) the maximum cross-sectional area in m^2 units of the spray-drying tower is in the range of from $3gm^{-2}s^{-1}$ to $3,000gm^{-2}s^{-1}$, preferably from $20gm^{-2}s^{-1}$, or from $40gm^{-2}s^{-1}$, or even from $60gm^{-2}s^{-1}$, and preferably to $2,000gm^{-2}s^{-1}$, or to $1,000gm^{-2}s^{-1}$, or to $500gm^{-2}s^{-1}$, or to $250gm^{-2}s^{-1}$, or even to $150gm^{-2}s^{-1}$. This is especially preferred in order to control the residency time of the aqueous slurry in the spray-drying tower so as to ensure adequate drying time. This is even more preferred when it is desirable to spray-dry at lower air temperatures.

Spray-dried detergent powder. The spray-dried detergent powder has a bulk density of 426g/l or less, preferably from 100g/l, and preferably of 400g/l or less, or 300g/l or less, or even 200g/l or less. The method for determining the bulk density of the spray-dried powder is described in more detail below.

Typically, the spray-dried detergent powder comprises anionic detersive surfactant, from 0wt% to 10wt% zeolite builder, from 0wt% to 10wt% phosphate builder, preferably from 0wt% to 10wt% silicate salt. Typically, the spray-dried detergent powder comprises a

polymeric carboxylate and carbonate salt. The anionic detersive surfactant, zeolite builder, phosphate builder, silicate salt, polymeric carboxylate, and carbonate salt are described in more detail below.

Typically, the spray-dried detergent powder is suitable for use as, or for incorporation into, a solid laundry detergent composition. The spray-dried powder can be admixed with other detergent ingredients, such as dry-added sodium percarbonate, anionic detersive surfactant agglomerates, enzymes or other spray-dried powders, to form a solid laundry detergent composition.

Typically, the spray-dried detergent powder comprises a polymeric component and a non-polymeric component. The polymeric component and non-polymeric component are described in more detail below. Typically, and even preferably, the spray-dried detergent powder comprises an inorganic component and an organic component. The inorganic component and organic component are described in more detail below.

Aqueous slurry. The aqueous slurry is suitable for spray-drying. The aqueous slurry comprises from 30wt% to 60wt% water, preferably from 35wt%, or from 40wt%, or from 45wt%, or even from 50wt% water, and preferably to 55wt% water. The aqueous slurry comprises from 40wt% to 70wt% non-aqueous material, preferably from 45wt%, and preferably to 65wt%, or to 60wt%, or to 55wt%, or even to 50wt% non-aqueous material. The non-aqueous material means any material that is not water. The non-aqueous material is described in more detail below.

The aqueous slurry has a viscosity of from 0.2Pas to 2.0Pas, when measured at a shear rate of $1,000s^{-1}$ and at a temperature of 70°C.

Non-aqueous material. The non-aqueous material is any material that is not water. The non-aqueous material typically comprises an inorganic component and an organic component. The inorganic component and organic component are described in more detail below. Typically, the non-aqueous material comprises an inorganic component and organic component in a weight ratio of from 0.1:1 to 10:1, preferably from 0.2:1, or even from 0.3:1, and preferably to 5:1, or to 3:1, or to 1.5:1, or to 1.2:1, or to 1.0:1, or to 0.8:1, or even to 0.5:1.

The non-aqueous material typically comprises a polymeric component and a non-polymeric component.

Typically, the non-aqueous material comprises anionic detersive surfactant, polymeric carboxylate and carbonate salt. The anionic detersive surfactant, polymeric carboxylate, and carbonate salt are described in more detail below. It may be preferred that the non-aqueous material comprises from 0wt% to 5wt% alkyl alkoxylated sulphate anionic detersive surfactant, preferably to 4wt%, or to 3wt%, or to 2wt%, or to 1wt% alkyl alkoxylated sulphate anionic detersive surfactant.

It may even be preferred that the non-aqueous material comprises essentially no alkyl alkoxylated sulphate anionic detersive surfactant; by comprises essentially no alkyl alkoxylated sulphate anionic detersive surfactant it is meant that the non-aqueous material comprises no deliberately added alkyl alkoxylated sulphate anionic detersive surfactant. This is especially preferred if the non-aqueous material comprises an alkyl benzene sulphonate anionic detersive surfactant.

Typically, the non-aqueous material comprises from 0wt% to 10wt% zeolite builder, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% zeolite builder. It may even be preferred for the non-aqueous material to be essentially free from zeolite builder. By essentially free from zeolite builder it is typically meant that the non-aqueous material comprises no deliberately added zeolite builder.

Typically, the non-aqueous material comprises from 0wt% to 10wt% phosphate builder, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% phosphate builder. It may even be preferred for the non-aqueous material to be essentially free from phosphate builder. By essentially free from phosphate builder it is typically meant that the non-aqueous material comprises no deliberately added phosphate builder.

Typically, the non-aqueous material comprises from 0wt% to 10wt% silicate salt, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% silicate salt. It may even be preferred for the non-aqueous material to be essentially free from silicate salt. By essentially free from silicate salt it is typically meant that the non-aqueous material comprises no deliberately added silicate salt.

Inorganic component: For the purpose of the present invention, inorganic component is defined as any material that does not comprise a hydrocarbon moiety. Examples of inorganic component include sodium carbonate and sodium sulphate.

Organic component: For the purpose of the present invention, organic component is defined as any material that comprises a hydrocarbon moiety. For the purpose of the present invention, a hydrocarbon moiety comprises a carbon atom that is covalently bonded to a hydrogen atom: i.e. having the general formula:



Examples of organic component include alkyl benzene sulphonate and citric acid.

Polymeric component. For the purpose of the present invention, the polymeric component is defined as any material that comprises at least four monomer units and has a molecular weight of 1,000 Da or greater.

Non-polymeric component. For the purpose of the present invention, the non-polymeric component is defined as any material that comprises less than four monomer units and/or has a molecular weight of less than 1,000 Da.

Anionic detersive surfactant: The spray-dried powder typically comprises from 1wt% to 70wt% anionic detersive surfactant, preferably from 2wt%, or from 5wt%, or from 7wt%, or even from 10wt%, and preferably to 60wt%, or to 50wt%, or to 40wt%, or even to 30wt% anionic detersive surfactant. Suitable anionic detersive surfactants are alkoxylated alcohol sulphate anionic detersive surfactants such as linear or branched, substituted or unsubstituted ethoxylated $C_{12\text{-}18}$ alcohol sulphates having an average degree of ethoxylation of from 1 to 10, preferably from 3 to 7. Other suitable anionic detersive surfactant are alkyl benzene sulphonate anionic detersive surfactants such as linear or branched, substituted or unsubstituted $C_{8\text{-}18}$ alkyl benzene sulphonates, preferably linear unsubstituted $C_{10\text{-}13}$ alkyl benzene sulphonates. Other suitable anionic detersive surfactants are alkyl sulphates, alkyl sulphonates, alkyl phosphates, alkyl phosphonates, alkyl carboxylates or any mixture thereof.

Polymeric carboxylate. The spray-dried powder preferably comprises polymeric carboxylate. It may be preferred for the spray-dried powder to comprise at least 1wt%, or at least 2wt%, or at least 3wt%, or at least 4wt%, or even at least 5wt% polymeric carboxylate. The polymeric carboxylate can sequester free calcium ions in the wash liquor. The polymeric

carboxylate can also act as a soil dispersant and can provide an improved particulate stain removal cleaning benefit. Preferred polymeric carboxylates include: polyacrylates, preferably having a weight average molecular weight of from 1,000Da to 20,000Da; co-polymers of maleic acid and acrylic acid, preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 1:1 to 1:10 and a weight average molecular weight of from 10,000Da to 200,000Da, or preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 0.3:1 to 3:1 and a weight average molecular weight of from 1,000Da to 50,000Da.

Carbonate salt. The spray-dried powder typically comprises carbonate salt, typically from 1wt% to 50wt%, or from 5wt% to 25wt% or from 10wt% to 20wt% carbonate salt. A preferred carbonate salt is sodium carbonate and/or sodium bicarbonate. A highly preferred carbonate salt is sodium carbonate. Preferably, the spray-dried powder may comprise from 10wt% to 40wt% sodium carbonate. However, it may also be preferred for the spray-dried powder to comprise from 2wt% to 8wt% sodium bicarbonate. Sodium bicarbonate at these levels provides good alkalinity whilst minimizing the risk of surfactant gelling which may occur in surfactant-carbonate systems. If the spray-dried powder comprises sodium carbonate and zeolite builder, then preferably the weight ratio of sodium carbonate to zeolite builder is at least 15:1.

The carbonate salt, or at least part thereof, is typically in particulate form, typically having a weight average particle size in the range of from 200 to 500 micrometers. However, it may be preferred for the carbonate salt, or at least part thereof, to be in micronised particulate form, typically having a weight average particle size in the range of from 4 to 40 micrometers; this is especially preferred when the carbonate salt, or at least part thereof, is in the form of a co-particulate admixture with a detersive surfactant, such as the alkyl benzene sulphonate, or alternatively with an alkoxylated anionic detersive surfactant.

High levels of carbonate improve the cleaning performance of the spray-dried powder by increasing the pH of the wash liquor. This increased alkalinity: improves the performance of the bleach, if present; increases the tendency of soils to hydrolyze, which facilitates their removal from the fabric; and also increases the rate, and degree, of ionization of the soils to be cleaned (n.b. ionized soils are more soluble and easier to remove from the fabrics during the washing stage of the laundering process). In addition, high carbonate levels improve the flowability of the spray-dried powder.

Zeolite builder: The spray-dried detergent powder typically comprises from 0wt% to 10wt% zeolite builder, preferably to 8wt%, or to 6wt%, or to 5wt%, or to 4wt% or to 2wt% zeolite builder. It may even be preferred for the spray-dried detergent powder to be essentially free from zeolite builder. By essentially free from zeolite builder it is typically meant that the spray-dried detergent powder comprises no deliberately added zeolite builder. This is especially preferred if it is desirable for the spray-dried detergent powder to be very highly water-soluble, to minimize the amount of water-insoluble residues (for example, which may deposit on fabric surfaces), and also when it is highly desirable to have transparent wash liquor. Zeolite builders include zeolite A, zeolite X, zeolite P and zeolite MAP.

Phosphate builder: The spray-dried detergent powder typically comprises from 0wt% to 10wt% phosphate builder, preferably to 8wt%, or to 6wt%, or to 5wt%, or to 4wt% or to 2wt% phosphate builder. It may even be preferred for the spray-dried detergent powder to be essentially free from phosphate builder. By essentially free from phosphate builder it is typically meant that the spray-dried detergent powder comprises no deliberately added phosphate builder. This is especially preferred if it is desirable for the spray-dried detergent powder to have a very good environmental profile. Phosphate builders include sodium tripolyphosphate.

Silicate salt: The spray-dried detergent powder preferably comprises from 0wt% to 10wt% silicate, preferably to 8wt%, or 6wt%, or to 4wt% or to 2wt% silicate salt. It may even be preferred for the spray-dried detergent powder to be essentially free from silicate salt. By essentially free from silicate salt it is typically meant that the spray-dried detergent powder comprises no deliberately added silicate salt. This is especially preferred in order to ensure that the spray-dried detergent powder has a very good dispensing and dissolution profiles and to ensure that the spray-dried detergent powder provides a clear wash liquor upon dissolution in water. Silicate salts include water-insoluble silicates. Silicate salts include amorphous silicates and crystalline layered silicates (e.g. SKS-6). A typical silicate salt is sodium silicate.

Other detergent ingredients: The spray-dried powder, and the non-aqueous component of the aqueous slurry, typically comprises detergent ingredients. Suitable detergent ingredients include: detersive surfactants such as anionic detersive surfactants, nonionic

detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants; preferred non-ionic detersive surfactants are C_{8-18} alkyl alkoxylated alcohols having an average degree of alkoxylation of from 1 to 20, preferably from 3 to 10, most preferred are C_{12-18} alkyl ethoxylated alcohols having an average degree of alkoxylation of from 3 to 10; preferred cationic detersive surfactants are mono-C_{6-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides, more preferred are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C_{10-12} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride; source of peroxygen such as percarbonate salts and/or perborate salts, preferred is sodium percarbonate, the source of peroxygen is preferably at least partially coated, preferably completely coated, by a coating material such as a carbonate salt, a sulphate salt, a silicate salt, borosilicate, or mixtures, including mixed salts, thereof; bleach activator such as tetraacetyl ethylene diamine, oxybenzene sulphonate bleach activators such as nonanoyl oxybenzene sulphonate, caprolactam bleach activators, imide bleach activators such as N-nonanoyl-N-methyl acetamide, preformed peracids such as N,N-pthaloylamino peroxycaproic acid, nonylamido peroxyadipic acid or dibenzoyl peroxide; carbonate salts, preferably sodium carbonate and/or sodium bicarbonate, preferably sodium carbonate; polymeric carboxylates, preferably co-polymers of maleic acid and acrylic acid and salts thereof; enzymes such as amylases, carbohydrases, cellulases, laccases, lipases, oxidases, peroxidases, proteases, pectate lyases and mannanases; suds suppressing systems such as silicone based suds suppressors; fluorescent whitening agents; photobleach; filler salts such as sulphate salts, preferably sodium sulphate; fabric-softening agents such as clay, silicone and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4-vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as hydrophobically modified cellulose and oligomers produced by the condensation of imidazole and epichlorhydrin; soil dispersants and soil anti-redeposition aids such as alkoxylated polyamines and ethoxylated ethyleneimine polymers; anti-redeposition components such as carboxymethyl cellulose and polyesters; perfumes; sulphamic acid or salts thereof; citric acid or salts thereof; and dyes such as orange dye, blue dye, green dye, purple dye, pink dye, or any mixture thereof.

Preferably, the composition comprises less than 1wt% chlorine bleach and less than 1wt% bromine bleach. Preferably, the composition is essentially free from bromine bleach and

chlorine bleach. By "essentially free from" it is typically meant "comprises no deliberately added".

Method for determining the bulk density of the spray-dried powder. The bulk density is typically determined by the following method:

Summary: A 500 ml graduated cylinder is filled with a powder, the weight of the sample is measured and the bulk density of the powder is calculated in g/l.

Equipment:

1. Balance. The balance has a sensitivity of 0.5g.

2. Graduated cylinder. The graduated cylinder has a capacity 500ml. The cylinder should be calibrated at the 500ml mark, by using 500g of water at 20°C. The cylinder is cut off at the 500ml mark and ground smooth.

3. Funnel. The funnel is cylindrical cone, and has a top opening of 110mm diameter, a bottom opening of 40mm diameter, and sides having a slope of 76.4° to the horizontal.

4. Spatula. The spatula is a flat metal piece having of a length of at least 1.5 times the diameter of the graduated cylinder.

5. Beaker. The beaker has a capacity of 600ml.

6. Tray. The tray is either a metal or plastic square, is smooth and level, and has a side length of at least 2 times the diameter of the graduated cylinder.

7. Ring stand.

8. Ring clamp.

9. Metal gate. The metal gate is a smooth circular disk having a diameter of at least greater than the diameter of the bottom opening of the funnel.

Conditions: The procedure is carried out indoors at conditions of 20°C temperature, 1 x $10^5 Nm^{-2}$ pressure and a relative humidity of 25%.

Procedure:

1. Weigh the graduated cylinder to the nearest 0.5g using the balance. Place the graduated cylinder in the tray so that it is horizontal with the opening facing upwards.

2. Support the funnel on a ring clamp, which is then fixed to a ring stand such that the top of the funnel is horizontal and rigidly in position. Adjust the height of the funnel so that its bottom position is 38mm above the top centre of the graduated cylinder.

3. Support the metal gate so as to form an air-tight closure of the bottom opening of the funnel.

4. Completely fill the beaker with a 24 hour old powder sample and pour the powder sample into the top opening of the funnel from a height of 2cm above the top of the funnel.

5. Allow the powder sample to remain in the funnel for 10 seconds, and then quickly and completely remove the metal gate so as to open the bottom opening of the funnel and allow the powder sample to fall into the graduated cylinder such that it completely fills the graduated cylinder and forms an overtop. Other than the flow of the powder sample, no other external force, such as tapping, moving, touching, shaking, etc, is applied to the graduated cylinder. This is to minimize any further compaction of the powder sample.

6. Allow the powder sample to remain in the graduated cylinder for 10 seconds, and then carefully remove the overtop using the flat edge of the spatula so that the graduated cylinder is exactly full. Other than carefully removing the overtop, no other external force, such as tapping, moving, touching, shaking, etc, is applied to the graduated cylinder. This is to minimize any further compaction of the powder sample.

7. Immediately and carefully transfer the graduated cylinder to the balance without spilling any powder sample. Determine the weight of the graduated cylinder and its powder sample content to the nearest 0.5g.

8. Calculate the weight of the powder sample in the graduated cylinder by subtracting the weight of the graduated cylinder measured in step 1 from the weight of the graduated cylinder and its powder sample content measured in step 7.

9. Immediately repeat steps 1 to 8 with two other replica powder samples.

10. Determine the mean weight of all three powder samples.

11. Determine the bulk density of the powder sample in g/l by multiplying the mean weight calculated in step 10 by 2.0.

EXAMPLES

Example 1. A spray-dried laundry detergent powder and process of making it.

Aqueous slurry composition.

Component	%w/w Aqueous slurry
Linear alkyl benzene sulphonate	10.6
Acrylate/maleate copolymer	4.6
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	1.4
Sodium carbonate	19.4
Sodium sulphate	28.6
Water	34.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	1.4
Total Parts	**100.00**

Preparation of a spray-dried laundry detergent powder.

An aqueous slurry having the composition as described above is prepared having a moisture content of 34.0%. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. At the end of preparation, the aqueous slurry is heated to 80°C and pumped under pressure ($5x10^6 Nm^{-2}$), into a counter current spray-drying tower with an air inlet temperature of from 290°C. The aqueous slurry is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.15mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 2.0wt%, a bulk density of 310g/l and a particle size distribution such that greater than 90wt% of the spray-dried powder has a particle size of from 150 to 710 micrometers. The composition of the spray-dried powder is given below.

Spray-dried laundry detergent powder composition.

Component	%w/w Spray Dried Powder
Linear alkyl benzene sulphonate	15.8
Acrylate/maleate copolymer	6.8
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	2.1
Sodium carbonate	28.7
Sodium sulphate	42.4
Water	2.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	2.2
Total Parts	**100.00**

Example 2. A spray dried laundry detergent powder and process of making it.

Aqueous slurry composition.

Component	%w/w Aqueous slurry
Linear alkyl benzene sulphonate	21.3
Acrylate/maleate copolymer	9.4
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	1.7
Sodium carbonate	18.8
Carboxy-methyl-cellulose polymer	4.3
Water	42.0
Miscellaneous such as magnesium sulphate, brightener, and one or more stabilizers	2.5
Total Parts	**100.00**

Preparation of a spray-dried laundry detergent powder.

An aqueous slurry having the composition as described above is prepared having a moisture content of 42.0%. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. At the end of preparation, the

aqueous slurry is heated to 85°C and pumped under pressure (from $6.5x10^6 Nm^{-2}$), into a counter current spray-drying tower with an air inlet temperature of from 275°C. The aqueous slurry is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.15mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 3.0wt%, a bulk density of 250g/l and a particle size distribution such that greater than 90wt% of the spray-dried powder has a particle size of from 150 to 710 micrometers. The composition of the spray-dried powder is given below.

Spray-dried laundry detergent powder composition.

Component	**%w/w Spray Dried Powder**
Linear alkyl benzene sulphonate	35.7
Acrylate/maleate copolymer	15.7
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	2.9
Sodium carbonate	31.4
Carboxy-methyl-cellulose polymer	7.1
Water	3.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	4.2
Total Parts	**100.00**

CLAIMS

1. A spray-drying process for the preparation of a spray-dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0wt% to 10wt% zeolite builder and from 0wt% to 10wt% phosphate builder, and wherein the process comprises the step of:

(a) preparing an aqueous slurry suitable for spray-drying comprising from 30wt% to 60wt% water and from 40wt% to 70wt% non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component, wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3:1 to 5:1; and

(b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65°C to 140°C, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70°C to 120°C.

2. A process according to claim 1, wherein the aqueous slurry comprises from 40wt% to 50wt% water and from 50wt% to 60wt% non-aqueous material.

3. A process according to any preceding claim, wherein the spray-dried detergent powder has a bulk density of 325g/l or less.

4. A process according to any preceding claim, wherein the air flow rate in the spray-drying tower is in the range of from $15m^3s^{-1}$ to $30m^3s^{-1}$, wherein the maximum cross-sectional area of the spray-drying tower is in the range of from $20m^2$ to $40m^2$,
and wherein the ratio of (i) the air flow rate in m^3s^{-1} units in the spray-drying tower to (ii) the maximum cross sectional area of the spray-drying tower in m^2 units is in the range of from $0.2ms^{-1}$ to $1.0ms^{-1}$.

5. A process according to any preceding claim, wherein the slurry is sprayed into the spray-drying tower through a nozzle having an aperture having a diameter in the range of from 3mm to 4mm.

6. A process according to any preceding claim, wherein the slurry is sprayed into the spray-drying tower at a pressure in the range of from 5.0 x 10^6 Nm^{-2} to 7.0 x 10^6 Nm^{-2}.

7. A process according to any preceding claim, wherein the ratio of (i) the rate in gs^{-1} units at which the aqueous slurry is sprayed into the spray-drying tower to (ii) the maximum cross-sectional area in m^2 units of the spray-drying tower is in the range of from 40 to 250$gm^{-2}s^{-1}$.

8. A process according to any preceding claim, wherein the non-aqueous material comprises anionic surfactant, polymeric carboxylate and carbonate salt, wherein:

(a) the weight ratio of anionic surfactant to polymeric carboxylate is in the range of from 2:1 to 3:1;

(b) the weight ratio of carbonate salt to anionic surfactant is in the range of from 0.5:1 to 2:1; and

(c) the weight ratio of carbonate salt to polymeric carboxylate is in the range of from 1.5:1 to 4:1.

9. A process according to any preceding claim, wherein the non-aqueous material comprises alkyl benzene sulphonate anionic detersive surfactant.

10. A process according to any preceding claim, wherein the non-aqueous material comprises from 0wt% to 4wt% silicate salt.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/054198

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D11/00 C11D11/02 C11D17/06 C11D1/02 C11D3/02
C11D3/10
ADD. C11D1/22
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2 298 650 A1 (SAMARAS NICHOLAS N T ET AL) 13 October 1942 (1942-10-13) claim 1 examples I,III * page 4, column 1, line 66 - page 4, column 2, line 5 *	1-4,6,7, 9,10
X	US 3 816 352 A1 (LOUREIRO V ET AL) 11 June 1974 (1974-06-11) claims example 1 column 3, line 23 - line 30	1-4,6,7, 9,10
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2006)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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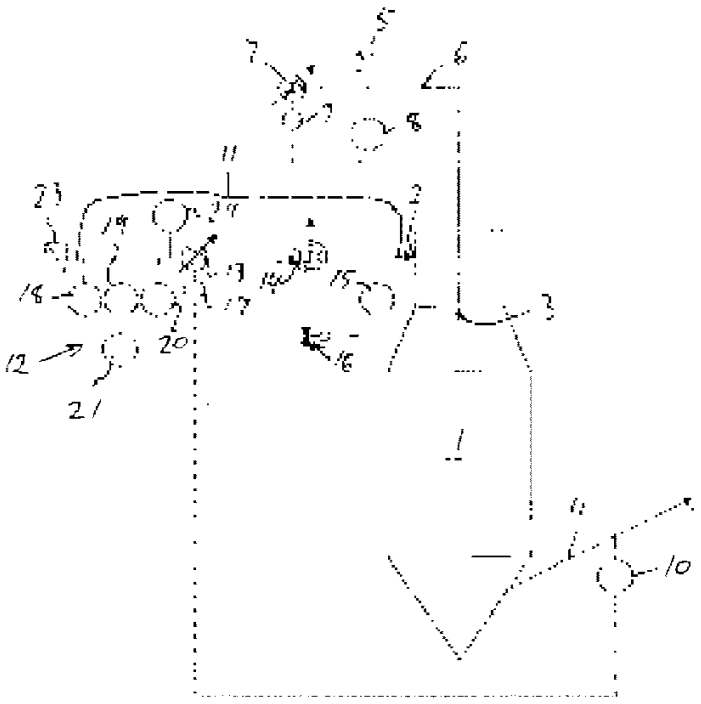
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(54) **Title:** A METHOD OF CONTROLLING A SPRAY DRYER APPARATUS BY REGULATING AN INLET AIR FLOW RATE, AND A SPRAY DRYER APPARATUS



(57) **Abstract:** A method of controlling a spray dryer apparatus having a spray dryer chamber (1), an air inlet (2), an inlet air control system (11) including a fan (13) and an air heater (14), a feed inlet (3), and an exhaust air outlet (4), comprising determining a content (Y) of moisture of inlet air, determining an inlet air temperature set value (T_{inlet}) in dependence of the inlet air moisture content (Y), determining an inlet air temperature measured value of inlet air between the air heater (14) and the spray dryer chamber (1), and regulating the inlet air temperature in dependence of the inlet air temperature set value and the inlet air temperature measured value, and determining an outlet air temperature of the exhaust air and regulating an inlet air flow rate in dependence of the outlet air temperature.

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A method of controlling a spray dryer apparatus by regulating an inlet air flow rate, and a spray dryer apparatus.

The present invention relates to a method of controlling a spray dryer apparatus having a spray dryer chamber, an air inlet, an inlet air control system including a fan and an air heater, a feed inlet, and an exhaust air outlet.

The invention further relates to a spray dryer apparatus.

Spray dryers are used for drying a feed comprising solids and a solvent e.g. water by spraying the feed in form of droplets into a spray dryer chamber. In the spray dryer chamber the spray is meet by an, often hot, inlet air flow causing the solvent to evaporate. A dried product in form of a powder with residual moisture content can thereafter be collected from the apparatus.

The quality and efficiency of the spray drying process is depending on several parameters such as: The pattern of the spray including i.a. the distribution of smaller and bigger droplets, the pattern of the air flow in the spray dryer chamber, the inlet air temperature, the feed rate, the inlet air flow rate etc.

Apart from the dried product, exhaust air containing evaporated solvent is a product of the drying process, and parameters such as the outlet air temperature of the exhaust air and the relative humidity of the exhaust air are normally used to design the drying process. The outlet temperature is measured during the process and is generally known to be closely related to the condition of the dried product.

Thus it is normal practice to control the operation of a spray dryer apparatus on basis of measurements of the outlet air temperature.

Two different methods of control are used in the art namely:

Maintaining a set outlet air temperature by adjusting the feed rate to the dryer; or

Maintaining a set outlet temperature by adjusting the inlet air temperature.

The set outlet temperature may be kept constant in accordance with a value set a priori for a specific spray dryer apparatus and a

specific process, or the set outlet temperature may be adjusted during operation on basis of measurements of moisture content of the dried product (cf. Masters, K., *Spray Drying Handbook*, 5th ed., Chapter 10, London, Longman Scientific & Technical (1991)). From this reference it is further known that high ambient air relative humidity may necessitate a reduction of the inlet air temperature and thus a reduction of the capacity of the spray dryer apparatus, (pages 120-121).

The above-mentioned known methods of control have some disadvantages.

Adjusting the feed rate entails that the capacity of the spray dryer apparatus is not optimally utilised, and if the spray drying is a part of a larger process adjusting/lowering the feed rate may result in delays in the entire process. Further, adjusting the feed rate may influence the spray pattern and thus the powder characteristics in an undesirable manner.

Adjusting the inlet air temperature may not be acceptable e.g. if the required adjustment is an increase of the temperature and the inlet air temperature is already close to a limit not to be exceeded in order not to risk heat damaging the product.

In case of an increase of the moisture content of the ambient air, which in a usual spray drying process is heated and used as inlet air, the drying capacity decreases as mentioned above. Under such circumstances it is normal procedure to decrease the feed rate to compensate for the decreasing capacity.

A way of dealing with a fluctuating moisture content of the ambient air is to use a dehumidification equipment on the inlet air, but this is expensive and normally relevant for small capacity equipment only.

The object of the present invention is to provide a method of control, which at least to some degree avoids these disadvantages of the prior art. It is a further object to provide an apparatus suited for using such a method. It is a further object to provide a method of control and an apparatus allowing keeping nearby constant the outlet air temperature, the relative humidity of the outlet air and therewith the

residual moisture content of the dried product.

In a first aspect these objects are met according to the invention by a method of controlling a spray dryer apparatus having a spray dryer chamber, an air inlet, an inlet air control system including a fan and an air heater, a feed inlet, and an exhaust air outlet, comprising determining a content of moisture of inlet air, determining an inlet air temperature set value in dependence of the inlet air moisture content, determining an inlet air temperature measured value of inlet air between the air heater and the spray dryer chamber, and regulating the inlet air temperature in dependence of the inlet air temperature set value and the inlet air temperature measured value, and determining an outlet air temperature of the exhaust air and regulating an inlet air flow rate in dependence of the outlet air temperature. Adjusting the inlet air temperature according to changes in the inlet air moisture content makes it possible to keep as well the temperature as the relative humidity of outlet air constant, and adjusting the inlet air flow rate makes it possible to keep the feed rate constant, thus making it possible to run the spray dryer apparatus under substantially constant conditions to obtain a product with substantially constant specifications and quantity. The inlet air moisture content may e.g. be measured continuously, at intervals, preferably regular intervals, or at predetermined times.

The inlet air moisture content determined may be the moisture content of the ambient air. In such case, which will be the normal case, any moisture added to ambient air before it reaches the air inlet is taken into account when determining the inlet air temperature set value.

Preferably, determining an inlet air temperature set value in dependence of the inlet or ambient air moisture content comprises providing a priori for a specific spray dryer apparatus and for a specific product to be processed by the spray dryer apparatus an expression for the inlet air temperature set value in dependence of varying inlet or ambient air moisture content. Such expression may be presented as a table, a curve, an algorithm, etc.

The method preferably comprises displaying said expression to

an operator.

Preferably the method further comprises displaying to the operator at least one current operational parameter together with at least one limit of an acceptable range for said operational parameter. The operational parameter is preferably selected from a group comprising inlet air moisture content, ambient air moisture content, ambient air relative humidity, inlet air temperature measured value, inlet air temperature set value, inlet air flow rate, a fan speed, and outlet air temperature.

Thereby it is possible to give the operator an indication of the current state of operation of the spray dryer apparatus making it possible for the operator to decide whether the control strategy used is correct under the circumstances.

In a second aspect the objects of the invention is obtained by a spray dryer apparatus comprising a spray dryer chamber, a feed inlet, a feed control device, an air inlet, an inlet air control system and an exhaust air outlet with an outlet air temperature measuring device, said inlet air control system comprising a fan, an inlet air flow rate control device, an air heater with an air heater control device, and an inlet air temperature measuring device for measuring temperature of inlet air between the air heater and the spray dryer chamber, said spray dryer apparatus further comprising an inlet air moisture content measuring device, a controller for determining an inlet air temperature set value depending on the inlet air moisture content, a connection for forwarding said inlet air temperature set value to the air heater control device and a connection for forwarding an outlet temperature measured value from the outlet air temperature measuring device to the inlet air flow rate control device. Thereby an apparatus is obtained, which is able to operate in accordance to the method of the invention and thus to operate under substantially constant conditions to produce a product of substantially constant quality and quantity.

Preferably the inlet air moisture content measuring device is an ambient air moisture content measuring device, and preferably said device comprises a hygrometer, a thermometer, a barometer, and a

controller.

The air inlet flow rate control device may comprise the fan and a fan controller.

Preferably the apparatus is provided with a graphic display device for displaying to an operator at least a current value of an operational parameter such as inlet air moisture content, ambient air moisture content, ambient air relative humidity, inlet air temperature measured value, inlet air temperature set value, inlet air flow rate, a fan speed, or outlet air temperature.

The invention will be described in further detail in the following with reference to the schematic drawing, in which

Fig. 1 shows an apparatus according to the invention,

Fig. 2 shows a graphic representation of a working line for the apparatus and

Fig. 3 shows a variant of he apparatus shown in Fig. 1.

Fig. 1 shows a spray dryer apparatus comprising a spray dryer chamber 1 with an air inlet 2, a feed inlet 3 and an exhaust air outlet 4. Further the apparatus comprise an outlet for dried product not shown and possibly an integrated fluid bed for treatment of the dried product as it is known in the art.

The spray dryer apparatus comprises a feed control device 5 connected to the feed inlet 3 by a feed line 6 for controlling the rate of the feed. The feed control device 5 comprises a feed pump 7, a pressure gauge 8 and feed pump controller 9 for maintaining a set pressure in the feed line 6.

The feed inlet 3 may comprise any known atomizer for atomising the feed such as a nozzle or a rotary atomizer.

The exhaust air outlet is provided with an outlet air temperature measuring device 10.

The exhaust air outlet 4 may be connected to a dust collector or the like, as it is generally known in the art. Also the exhaust air outlet may be connected to an exhaust fan, which may be regulated to maintain a set pressure inside the spray dryer chamber 1, as it is also known in the art.

The spray dryer apparatus further comprises an inlet air control system or device 11, which comprises an ambient air moisture content measuring device 12, a fan 13, an air heater 14, an inlet air temperature measuring device 15, an air heater control device or controller 16 and a fan controller 17.

The air heater 14 is in the present embodiment an indirect air heater heating the inlet air via a heat exchanger. Alternatively a direct air heater may be used, as it is known in the art.

The ambient air moisture content measuring device 12 comprises in the present embodiment a hygrometer 18, a thermometer 19, a barometer 20 and a controller 21.

One or more of the controllers may be incorporated in the general control system of the spray dryer apparatus.

During operation the spray dryer apparatus is controlled as follows:

A working line is a priori established for the spray dryer apparatus and for the specific process to be run, considering i.a. the nature of the feed and the required specifications of the dried product. This working line represents the connection between the current moisture content of the ambient air Y and the inlet air temperature T_{inlet} that will provide the requested dried product specifications given the fact that a change of the ambient air moisture content will entail a change of the relative humidity and/or the temperature of the exhaust air, and thus a change of the specifications of the dried product, if the inlet temperature is not adjusted correspondingly.

The working line should take into account features of the actual spray dryer apparatus such as heat loss from the spray dryer chamber, whether the air heated is an indirect heater heating the air through a heat exchanger or a direct heater combusting a fuel such as natural gas directly in the inlet air thus providing additional moisture content to the inlet air, any supplementary air introduced into the spray dryer chamber etc. The latter could e.g. be fluidizing air, conditioning air, JET SWEEP™ air, air-broom air or the like.

Fig. 2 shows an example of a curve 22 of a working line, the

curve being shown in a coordinate system having Y (g water vapour per kg dry air) as abscissa and T_{inlet} (°C) as ordinate. The curve 22 is a straight line with a negative slope and represents a case of indirect heating. In case of direct heating the slope would have been steeper due to the water supplied by the combustion.

A feed rate is set and the feed pump controller 9 regulates the feed pump 7 to maintain a constant pressure in the feed line 6 that will provide the set feed rate.

The current moisture content of the ambient air is determined in that measurements of the hygrometer 18 (measuring relative humidity), the thermometer 19 and the barometer 20 are feed to the controller 21, which on basis of these measurements establishes the content Y (g water vapour per kg dry air) of moisture in the air. This may be established in any known manner e.g. by utilising a Psychrometric or Mollier chart.

The controller 21 establishes an inlet air temperature set value on basis of the working line and feeds said value to the air heater controller 16.

The fan 13 sucks air through a filter 23, past measuring points of the hygrometer 18, the thermometer 19, and the barometer 20, and blows it through the air heater, past a measuring point of the inlet air temperature measuring device 15, and through the air inlet 2 into the spray dryer chamber 1.

The measured inlet air temperature value is fed to the air heater controller 16 where it is compared with the inlet air temperature set value and the air heater controller regulates the supply of fuel to the heater on basis of the comparison to obtain a measured value of the temperature equal to the set value.

The value of the outlet air temperature as measured by the outlet temperature measuring device 10 is fed to the fan controller 17, where it is compared to an outlet air temperature set value. The fan controller 17 functions as an inlet air flow rate control device by controlling the speed of the fan 13 in response to the comparison between the set and the measured values of the outlet air temperature.

In case the measured value is lower than the set value the speed of the fan 13 is increased to increase the flow rate of inlet air and thus to increase the flow of heat energy into the spray dryer chamber 1 and vice versa.

In this way the outlet temperature is maintained substantially constant and as the feed rate is also maintained constant the rate of evaporation of the solvent of the feed (water) is by this method maintained substantially constant.

The shown embodiment of the apparatus further comprises a flow meter 24 measuring the flow rate of inlet air. Optionally the fan controller 17 may have an input from the flow meter 24 for assisting the control of the apparatus.

Fig. 3 shows a variant of the apparatus shown in Fig. 1 and similar items are referred to by similar reference numerals. Only the differences between the two embodiments will be explained in the following.

Whereas the inlet air control device 11 of the embodiment shown in Fig. 1 comprises a fan 13 blowing air into the spray dryer chamber 1, in the embodiment shown in Fig. 3 an inlet air control device or system 11' comprises a suction fan 13' situated at the exhaust air outlet 4 and a suction fan controller 17'. As by the embodiment shown in Fig. 1 a dust collector, not shown, may be connected to the exhaust air outlet 4. Such a dust collector may be placed upstream or downstream of the suction fan 13'.

As by the embodiment shown in Fig. 1, the value of the outlet air temperature as measured by the outlet temperature measuring device 10 is fed to the suction fan controller 17', where it is compared to an outlet air temperature set value. The suction fan controller 17' functions as an inlet air flow rate control device by controlling the speed of the suction fan 13' in response to the comparison between the set and the measured values of the outlet air temperature. In case the measured value is lower than the set value the speed of the suction fan 13' is increased to increase the flow rate of air through the spray dryer chamber 1 and thus the flow rate of inlet air thereby increasing the flow

of heat energy into the spray dryer chamber 1 and vice versa.

Below are given 4 examples of operation of a spray dryer apparatus according to the invention at different ambient air moisture contents:

Example 1

(Standard)

Ambient air moisture content: Y = 7g water/kg dry air,

Feed rate: FER= 4,110kg/h,

Outlet air temperature: T_{outlet} = 105°C,

Inlet air temperature: T_{inlet} = 250°C,

Inlet dry air flow rate: G = 37,956kg/h,

Relative volume inlet air: Load = 1

Example 2

Ambient air moisture content: Y = 4g water/kg dry air,

Feed rate: FER = 4,110kg/h,

Outlet air temperature: T_{outlet} = 105°C,

Inlet air temperature: T_{inlet} = 259°C,

Inlet dry air flow rate: G = 35,890kg/h,

Relative volume inlet air: Load = 0.951

Example 3

Ambient air moisture content: Y = 10g water/kg dry air,

Feed rate: FER = 4,110kg/h,

Outlet air temperature: T_{outlet} = 105°C,

Inlet air temperature: T_{inlet} = 241°C,

Inlet dry air flow rate: G = 40,269kg/h,

Relative volume inlet air: Load = 1.055

Example 4

Ambient air moisture content: Y = 15g water/kg dry air,

Feed rate: FER = 4,110kg/h,

Outlet air temperature: T_{outlet} = 105°C,

Inlet air temperature: T_{inlet} = 226°C,
Inlet dry air flow rate: G = 44,846kg/h,
Relative volume inlet air: Load = 1.164

These examples show how the inlet air temperature (T_{inlet}) is decreased and the inlet air flow rate (G), and together therewith the relative volume of inlet air (Load), is increased when the moisture content of the ambient air (Y) is increased and vice versa.

Fig. 2 shows the corresponding values of Y and T_{inlet} of the above examples 1-4, lying on the working line (curve 22).

According to the invention a figure like the one shown in fig. 2 may be shown on a graphic display of the spray dryer apparatus to indicate to an operator the state of operation of the spray dryer apparatus. Such a figure may also show limits 25 of a range for Y within which operation is acceptable and outside which operation is not acceptable or not possible. Thus it may be limited to which extent the inlet air flow rate may be adjusted e.g. the fan has a maximum capacity which cannot be exceeded. If Y is outside the acceptable range the operator may change the method of operation e.g. select a different feed rate, which will entail a different acceptable range for Y, or select another known method of regulation. If the spray drying process is an in line part of a larger process, selecting a different feed rate has the advantage that the changed flow of material through the spray dryer process is still constant, which makes it easier to regulate the larger process because variations of Y within certain limits will not cause variations of the larger process.

Further a figure shown on a graphic display to an operator may for the inlet air temperature T_{inlet} show the set value or the measured value. The set value will strictly follow the curve 22 whereas the measured value will due to delays in the regulation system be situated within a band surrounding the curve 22. Thus the figure may comprise lines 26 indicating acceptable variations of the measured value of the inlet air temperature from the set value. If the acceptable variations are exceeded it is an indication or warning for the operator that appropriate

action must be taken. Other or further measured parameters may be shown to the operator as possible warning, e.g. the ambient air relative humidity, the speed of the fan, etc.

For certain situations necessary actions may be taken automatically, e.g. selecting a different feed rate and working line, if Y exceeds a limit of the acceptable range. So this invention includes all automatic systems to perform the actions according to the method described.

The working line may be represented by a straight curve 22 as shown in fig. 2, but it may from experiences turn out that the correct relationship between Y and T_{inlet} that will maintain a given outlet air relative humidity for a given outlet air temperature, is nonlinear. The working line to be used in the method according to the invention should be based on such experiences with the feed in question and the actual spray dryer apparatus.

Different feeds need different working lines and thus the operator should be able to change the working line if the feed is changed, i.e. in case another product is to be dried.

Due to the constant feed rate obtained by the present invention, deposits may be kept at a minimum thus reducing the needs for maintenance. Further due to the constant process conditions a most homogeneous product may be obtained by method of the invention.

The scope of the present invention is not limited to the embodiments disclosed herein, but is defined in the claims. The skilled person will be able to suggest various modifications to the embodiment disclosed herein. Thus the air inlet system may be constructed differently from what is suggested herein and the regulation of the inlet air flow rate may be performed by other means than regulating the speed of a fan. Also e.g. the establishment of the moisture content of the ambient air may be performed in any conceivable way.

PATENT CLAIMS

1. A method of controlling a spray dryer apparatus having a spray dryer chamber, an air inlet, an inlet air control system including a fan and an air heater, a feed inlet, and an exhaust air outlet, comprising determining a content of moisture of inlet air, determining an inlet air temperature set value in dependence of the inlet air moisture content, determining an inlet air temperature measured value of inlet air between the air heater and the spray dryer chamber, and regulating the inlet air temperature in dependence of the inlet air temperature set value and the inlet air temperature measured value, and determining an outlet air temperature of the exhaust air and regulating an inlet air flow rate in dependence of the outlet air temperature.

2. A method according to claim 1, wherein the inlet air moisture content determined is the moisture content of the ambient air, and wherein any moisture added to ambient air before reaching the air inlet is taken into account when determining the inlet air temperature set value.

3. A method according to claim 1 or 2, wherein determining an inlet air temperature set value in dependence of the inlet air moisture content comprises providing a priori for a specific spray dryer apparatus and for a specific product to be processed by the spray dryer apparatus an expression for the inlet air temperature set value in dependence of varying inlet air moisture content.

4. A method according to any of the claims 1 to 3, wherein an automatic system is used to carry out said regulations.

5. A method according to claim 3, comprising displaying said expression to an operator.

6. A method according to any of the claims 1 to 5, comprising displaying to an operator at least one current operational parameter together with at least one limit of an acceptable range for said operational parameter.

7. A method according to claim 6, wherein said operational parameter is selected from a group comprising inlet air moisture content, ambient air moisture content, ambient air relative humidity,

inlet air temperature measured value, inlet air temperature set value, inlet air flow rate, a fan speed, and outlet air temperature.

8. A method according to any of the claims 1 to 5, wherein a feed flow through said feed inlet is kept constant unless the moisture content of the inlet air falls outside an acceptable range.

9. A spray dryer apparatus comprising a spray dryer chamber, a feed inlet, a feed control device, an air inlet, an inlet air control system and an exhaust air outlet with an outlet air temperature measuring device, said inlet air control system comprising a fan, an inlet air flow rate control device, an air heater with an air heater control device, and an inlet air temperature measuring device for measuring temperature of inlet air between the air heater and the spray dryer chamber, said spray dryer apparatus further comprising an inlet air moisture content measuring device, a controller for determining an inlet air temperature set value depending on the inlet air moisture content, a connection for forwarding said inlet air temperature set value to the air heater control device and a connection for forwarding an outlet temperature measured value from the outlet air temperature measuring device to the inlet air flow rate control device.

10. A spray dryer apparatus according to claim 9, wherein said inlet air moisture content measuring device is an ambient air moisture content measuring device.

11. A spray drying apparatus according to claim 9 or 10, wherein said inlet air moisture content measuring device comprises a hygrometer, a thermometer, a barometer, and a controller.

12. A spray drying apparatus according to any of claims 9 to 11, wherein the air inlet flow rate control device comprises said fan and a fan controller.

13. A spray dryer apparatus according to claim 12 wherein said fan is placed upstream of the spray dryer chamber.

14. A spray dryer apparatus according to claim 12 wherein said fan is a suction fan placed downstream of the spray dryer chamber.

15. A spray dryer apparatus according to any of the claims 9 to 14, comprising a graphic display device for displaying to an operator at

least a current value of an operational parameter.

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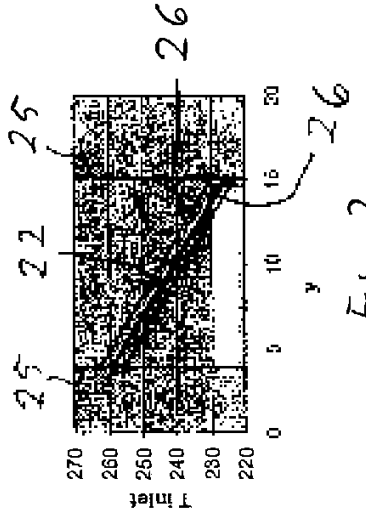

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Fig 2

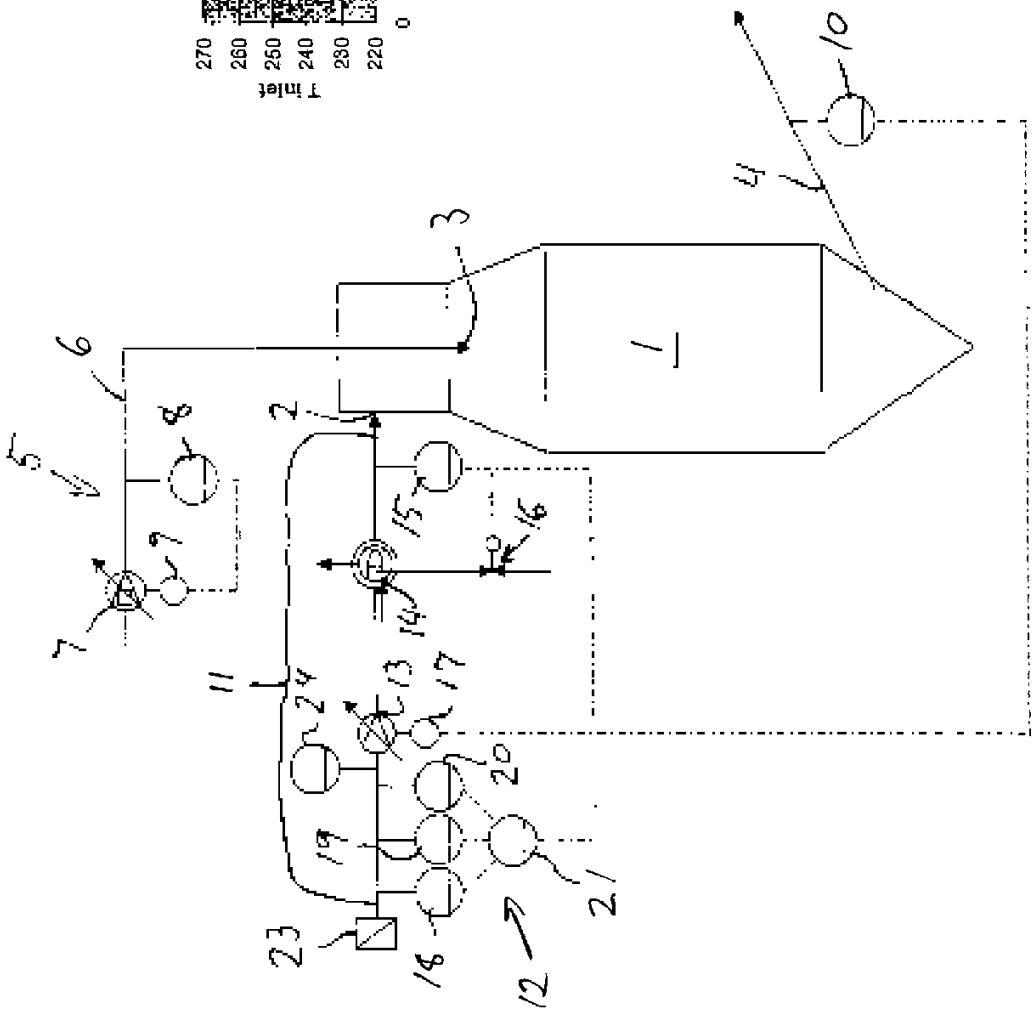

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Fig 1

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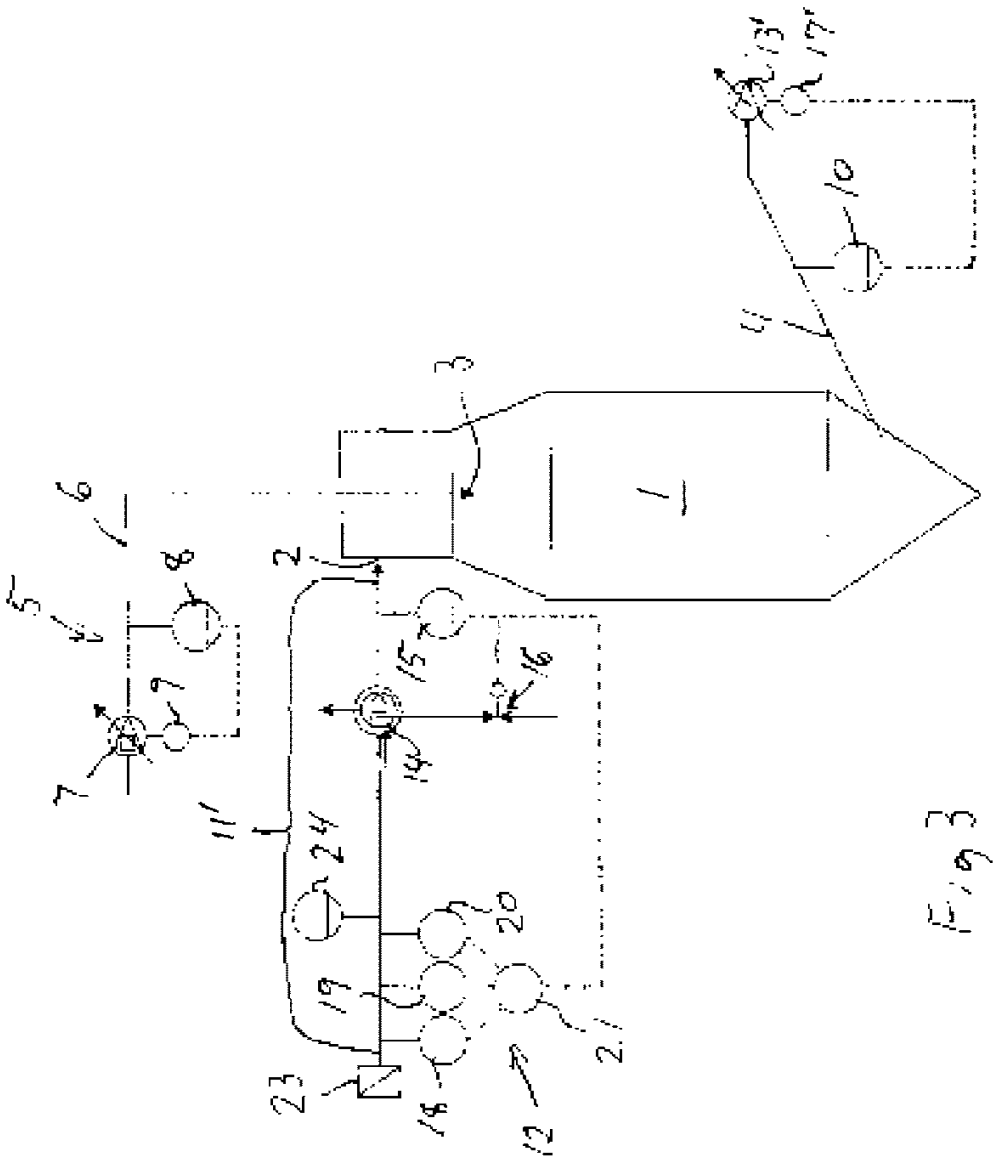


Fig 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2006/050081

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D1/16 F26B21/10 F26B21/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D F26B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 195 191 A1 (HOSOKAWA MICRON KK [JP]) 10 April 2002 (2002-04-10) paragraphs [0065], [0153] - [0155]; figure 14 -----	
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 August 2007	05/09/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rolder, Josef

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INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2006/050081

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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Information on patent family members

International application No
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WO 2010/104713 A1

(54) Title: A SPRAY-DRYING PROCESS

(57) Abstract: The present invention relates to a spray-drying process to prepare a spray-dried powder comprising: (a) anionic detersive surfactant; (b) from 0wt% to 10wt% zeolite builder; (c) from 0wt% to 10wt% phosphate builder; (d) optionally from 0wt% to 10wt% silicate salt; (e) optionally carbonate salt; (f) optionally polymeric material; and (g) optionally from 0wt% to 10wt% water, wherein, the process comprises the steps of: (i) spraying an aqueous slurry comprising: from (a) anionic detersive surfactant; (b) from 0wt% to 20wt% zeolite builder; (c) from 0wt% to 20wt% phosphate builder; (d) optionally from 0wt% to 20wt% silicate salt; (e) optionally carbonate salt; (f) optionally polymeric material; and (g) water, into a spray-drying zone, wherein the spray-drying zone is under negative pressure and wherein the air inlet air temperature into the spray-drying zone is greater than 150°C; and (ii) drying the aqueous slurry to form a spray-dried powder.

A SPRAY-DRYING PROCESS

FIELD OF THE INVENTION

The present invention relates to a spray-drying process for preparing a low built, highly soluble spray-dried powder that is suitable for incorporation into, or use as, a laundry detergent composition.

BACKGROUND OF THE INVENTION

Detergent manufacturers look to provide low density laundry detergent powders that have improved dissolution profiles at cooler washing temperatures, such as 30°C or 20°C. Water insoluble materials, most notably zeolite builders, have been removed, or their amount present in the powder has been significantly reduced.

Furthermore, there is also a need to ensure that the environmental profile of the laundry detergent powder is as optimal as possible. This bas meant that there is a trend for laundry detergent powder manufacturers to remove phosphate material, such as sodium tripolyphosphate (STPP) from the spray-dried powder.

The main process of preparing low density laundry detergent powder is to spray-dry an aqueous slurry comprising detergent ingredients. Typically, this involves spraying the aqueous slurry into a spray-drying tower that has hot air flowing through that then evaporates the water from the slurry droplets, forming spray-dried powder as the material falls down the tower.

However, the Inventors have found that when material such as zeolite and phosphate are removed from the solid content of the aqueous slurry, the temperature of the resultant spray-dried powder that is formed in the spray-drying zone has a tendency to over-heat and its temperature profile is difficult to control. The Inventors have found that the phenomenon of poor temperature control profile is a specific problem for these low built, highly soluble laundry detergent spray-dried powders and hasn't been observed to any appreciable degree before when spray-drying conventional laundry detergent powders.

The Inventors have found that this problem can be alleviated by running the spray-drying tower under a vacuum. The Inventors have found that by ensuring that the spray-drying zone is under a vacuum, i.e. such that the pressure in the spray-drying zone is negative. This ensures that ambient air is sucked into the spray-drying tower, which in turn provides a much need cooling effect on the spray-dried powder formed therein. The Inventors have found that controlling the

vacuum conditions in the spray-drying zone provides good temperature control of the resultant spray-dried powder.

SUMMARY OF THE INVENTION

The present invention provides a spray-drying process as defined in claim 1.

DETAILED DESCRIPTION OF THE INVENTION

Spray-drying process

The spray-drying process comprises the steps of: (i) spraying an aqueous slurry comprising into a spray-drying zone, wherein the spray-drying zone is under negative pressure and wherein the air inlet air temperature into the spray-drying zone is greater than 150°C; and (ii) drying the aqueous slurry to form a spray-dried powder. The aqueous slurry and spray-dried powder are described in more detail below.

Preferably, the spray-drying zone is under a pressure of at least -10Nm^{-2}, or at least -20Nm^{-2}, or at least -30Nm^{-2}, or at least -40Nm^{-2}, or at least -50Nm^{-2}, or at least -60Nm^{-2}, or at least -70Nm^{-2}, or at least -80Nm^{-2}, or at least -90Nm^{-2}, or at least -100Nm^{-2}, or at least -125Nm^{-2}, or at least -1500Nm^{-2}, or at least -175Nm^{-2}, or at least -200Nm^{-2}, or at least -250Nm^{-2}, or even at least -300Nm^{-2}. The higher the vacuum, the more ambient air is sucked into the bottom of the spray-drying tower and the greater the cooling effort is achieved. Typically, the maximum pressure one can use is determined by the structural strength of the spray-drying tower and care must be taken not to exceed this maximum vacuum so that no undue stress is placed on the spray-drying tower. Typically, pressures of up to -600Nm^{-2} or up to -500Nm^{-2} are preferably used.

Preferably, vacuum is controlled by controlling the speed and/or damper settings of the inlet and outlet air fans. For example, when setting up the spray-drying tower parameters, the inlet air fan (dilution air fan) is set to a fixed air flow rate. The speed or damper setting of the exhaust air fans is then adjusted accordingly to control the strength of the tower vacuum. Some spray-drying towers and production plants have a control loop to control the exhaust fans (and thereby the vacuum) which is normally activated about 5 minutes after start up. If more vacuum is needed the exhaust fans/dampers are adjusted accordingly. The negative pressure in the spray-drying tower can be measured by any available means. Typically pressure sensors are present in the spray-drying zone (inside the spray-drying tower).

The in-let air temperature into the spray-drying zone is preferably in the range of from greater than 150°C to 500°C, preferably from 200°C, or from 250°C, and preferably to 450°C or even to 400°C. The out-let (exhaust) air temperature is typically in the range of from 50°C to 150°C, preferably from 60°C, or 70°C or even 80°C, and preferably to 140°C, or to 130°C, or to 120°C, or to 110°C, or even to 100°C.

The temperature of the spray-dried powder exiting the spray-drying tower is typically in the range of from 50°C to 150°C, preferably from 60°C, or even from 70°C, and preferably to 140°C, or to 130°C, or to 120°C, or to 110°C, or even to 100°C. Preferably the spray-dried powder exiting the spray-drying tower has a temperature of less than 150°C, preferably less than 140°C, or less than 130°C, or less than 120°C, or less than 110°C, and preferably less than to 100°C.

The spray-dried powder typically exits the spray-drying zone (e.g. falls from the spray-drying tower) onto a conveyor belt, where other ingredients (such as percarbonate particles) are dry-added to the powder to form a laundry detergent composition.

Aqueous slurry

The aqueous slurry comprises (a) anionic detersive surfactant; (b) from 0wt% to 20wt% zeolite builder; (c) from 0wt% to 20wt% phosphate builder; (d) optionally from 0wt% to 20wt% silicate salt; (e) optionally carbonate salt; (f) optionally polymeric material; and (g) water. The aqueous slurry may comprise other detergent adjunct ingredients.

Preferably, the aqueous slurry comprises less than 15wt%, or less than 10wt%, or even less than 5wt% zeolite builder. Preferably the aqueous slurry is essentially free of zeolite builder. By essentially free it is typically meant herein as meaning no deliberately added.

Preferably, the aqueous slurry comprises less than 15wt%, or less than 10wt%, or even less than 5wt% phosphate builder. Preferably the aqueous slurry is essentially free of phosphate builder. By essentially free it is typically meant herein as meaning no deliberately added.

Spray-dried powder

The spray-dried powder comprises: (a) anionic detersive surfactant; (b) from 0wt% to 10wt% zeolite builder; (c) from 0wt% to 10wt% phosphate builder; (d) optionally from 0wt% to 10wt% silicate salt; (e) optionally carbonate salt; (f) optionally polymeric material; and (g) optionally from 0wt% to 10wt% water,

The spray-dried powder preferably comprises: (a) from 0wt% to 2wt% zeolite builder; (b) from 0wt% to 2wt% phosphate builder; and (c) optionally, from 0wt% to 2wt% silicate salt.

Preferably, the spray-dried powder comprises less than 8wt%, or less than 6wt%, or even less than 4wt% zeolite builder. Preferably the spray-dried powder is essentially free of zeolite builder. By essentially free it is typically meant herein as meaning no deliberately added.

Preferably, the spray-dried powder comprises less than 8wt%, or less than 6wt%, or even less than 4wt% phosphate builder. Preferably the spray-dried powder is essentially free of phosphate builder. By essentially free it is typically meant herein as meaning no deliberately added.

It may be preferred for the spray-dried powder to comprise a silicate salt, preferably from 1wt% to 10wt% silicate salt.

Anionic detersive surfactant

The anionic detersive surfactant preferably comprises alkyl benzene sulphonate. Preferably the anionic detersive surfactant comprises at least 50%, preferably at least 55%, or at least 60%, or at least 65%, or at least 70%, or even at least 75%, by weight of the anionic detersive surfactant, of alkyl benzene sulphonate. Preferably the alkyl benzene sulphonate is a linear or branched, substituted or unsubstituted, C_{8-18} alkyl benzene sulphonate. This is the optimal level of the C_{8-18} alkyl benzene sulphonate to provide a good cleaning performance. The C_{8-18} alkyl benzene sulphonate can be a modified alkylbenzene sulphonate (MLAS) as described in more detail in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548. Highly preferred C8-18 alkyl benzene sulphonates are linear C_{10-13} alkylbenzene sulphonates. Especially preferred are linear C_{10-13} alkylbenzene sulphonates that are obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzenes (LAB); suitable LAB include low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®.

The anionic detersive surfactant may preferably comprise other anionic detersive surfactants. A preferred adjunct anionic detersive surfactant is a non-alkoxylated anionic detersive surfactant. The non-alkoxylated anionic detersive surfactant can be an alkyl sulphate, an alkyl phosphate, an alkyl phosphonate, an alkyl carboxylate or any mixture thereof. The non-

alkoxylated anionic surfactant can be selected from the group consisting of: C_{10}-C_{30} primary, branched chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula:

$$CH_3(CH_2)xCH_2\text{-}OSO_3^- M^+$$

wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations are sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9; C_{10}-C_{18} secondary (2,3) alkyl sulphates, typically having the following formulae:

$$CH_3(CH_2)_x(CH)CH_3 \quad \text{or} \quad CH_3(CH_2)_y(CH)CH_2CH_3$$

(with $OSO_3^- M^+$ on the (CH) group)

wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations include sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9, y is an integer of at least 8, preferably at least 9; C_{10}-C_{18} alkyl carboxylates; mid-chain branched alkyl sulphates as described in more detail in US 6,020,303 and US 6,060,443; methyl ester sulphonate (MES); alpha-olefin sulphonate (AOS); and mixtures thereof.

Another preferred anionic detersive surfactant is an alkoxylated anionic detersive surfactant. The presence of an alkoxylated anionic detersive surfactant in the spray-dried powder provides good greasy soil cleaning performance, gives a good sudsing profile, and improves the hardness tolerance of the anionic detersive surfactant system. It may be preferred for the anionic detersive surfactant to comprise from 1% to 50%, or from 5%, or from 10%, or from 15%, or from 20%, and to 45%, or to 40%, or to 35%, or to 30%, by weight of the anionic detersive surfactant system, of an alkoxylated anionic detersive surfactant.

Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl alkoxylated sulphate having an average degree of alkoxylation of from 1 to 30, preferably from 1 to 10. Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 1 to 10. Most preferably, the alkoxylated anionic detersive surfactant is a linear unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 3 to 7.

The alkoxylated anionic detersive surfactant, when present with an alkyl benzene sulphonate may also increase the activity of the alkyl benzene sulphonate by making the alkyl benzene sulphonate less likely to precipitate out of solution in the presence of free calcium cations. Preferably, the weight ratio of the alkyl benzene sulphonate to the alkoxylated anionic detersive surfactant is in the range of from 1:1 to less than 5:1, or to less than 3:1, or to less than 1.7:1, or even less than 1.5:1. This ratio gives optimal whiteness maintenance performance combined with a good hardness tolerance profile and a good sudsing profile. However, it may be preferred that the weight ratio of the alkyl benzene sulphonate to the alkoxylated anionic detersive surfactant is greater than 5:1, or greater than 6:1, or greater than 7:1, or even greater than 10:1. This ratio gives optimal greasy soil cleaning performance combined with a good hardness tolerance profile, and a good sudsing profile.

Suitable alkoxylated anionic detersive surfactants are: Texapan LESTTM by Cognis; Cosmacol AESTM by Sasol; BES151TM by Stephan; Empicol ESC70/UTM; and mixtures thereof.

Preferably, the anionic detersive surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of the anionic detersive surfactant, of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate. Preferably the anionic detersive surfactant is essentially free of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate. By "essentially free of" it is typically meant "comprises no deliberately added". Without wishing to be bound by theory, it is believed that these levels of unsaturated anionic detersive surfactants such as alpha-olefin sulphonate ensure that the anionic detersive surfactant is bleach compatible.

Preferably, the anionic detersive surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of alkyl sulphate. Preferably the anionic detersive surfactant is essentially free of alkyl sulphate. Without wishing to be bound by theory, it is believed that these levels of alkyl sulphate ensure that the anionic detersive surfactant is hardness tolerant.

Zeolite builder

Suitable zeolite builders include zeolite A, zeolite X, zeolite P and zeolite MAP.

Phosphate builder

Suitable phosphate builders include sodium tripolyphosphate.

Silicate salt

Suitable silicate salts include amorphous silicates and crystalline layered silicates (e.g. SKS-6). A preferred silicate salt is sodium silicate.

Carbonate salt

Suitable carbonate salts include sodium salts of carbonate and/or bicarbonate. A highly preferred carbonate salt is sodium carbonate.

Polymeric material

A preferred polymeric material is a polymeric carboxylate, such as a co-polymer of maleic acid and acrylic acid. However, other polymers may also be suitable, such as polyamines (including the ethoxylated variants thereof), polyethylene glycol and polyesters. Polymeric soil suspending aids and polymeric soil release agents are also particularly suitable.

Adjunct detergent ingredients

Suitable adjunct detergent ingredients include: detersive surfactants such as nonionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants; preferred nonionic detersive surfactants are C_{8-18} alkyl alkoxylated alcohols having an average degree of alkoxylation of from 1 to 20, preferably from 3 to 10, most preferred are C_{12-18} alkyl ethoxylated alcohols having an average degree of alkoxylation of from 3 to 10; preferred cationic detersive surfactants are mono-C_{6-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides, more preferred are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-$C_{10\,12}$ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride; source of peroxygen such as percarbonate salts and/or perborate salts, preferred is sodium percarbonate, the source of peroxygen is preferably at least partially coated, preferably completely coated, by a coating ingredient such as a carbonate salt, a sulphate salt, a silicate salt, borosilicate, or mixtures, including mixed salts, thereof; bleach activator such as

tetraacetyl ethylene diamine, oxybenzene sulphonate bleach activators such as nonanoyl oxybenzene sulphonate, caprolactam bleach activators, imide bleach activators such as N-nonanoyl-N-methyl acetamide, preformed peracids such as N,N-pthaloylamino peroxycaproic acid, nonylamido peroxyadipic acid or dibenzoyl peroxide; enzymes such as amylases, carbohydrases, cellulases, laccases, lipases, oxidases, peroxidases, proteases, pectate lyases and mannanases; suds suppressing systems such as silicone based suds suppressors; fluorescent whitening agents; photobleach; filler salts such as sulphate salts, preferably sodium sulphate; fabric-softening agents such as clay, silicone and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4-vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as hydrophobically modified cellulose and oligomers produced by the condensation of imidazole and epichlorhydrin; soil dispersants and soil anti-redeposition aids such as alkoxylated polyamines and ethoxylated ethyleneimine polymers; anti-redeposition components such as carboxymethyl cellulose and polyesters; perfumes; sulphamic acid or salts thereof; citric acid or salts thereof; and dyes such as orange dye, blue dye, green dye, purple dye, pink dye, or any mixture thereof.

Preferably, no bleach adjunct ingredients, such as sodium percarbonate and/or sodium perborate, are spray-dried. Typically, these adjunct detergent ingredients are dry-added to the spray-dried powder and are not subjected to the higher temperatures and vacuum of the above described spray-drying process.

EXAMPLES

Example 1. A spray-dried laundry detergent powder and process of making it.

Aqueous slurry composition.

Component	%w/w Aqueous slurry
Linear alkyl benzene sulphonate	10.6
Acrylate/maleate copolymer	4.6
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	1.4
Sodium carbonate	19.4

Sodium sulphate	28.6
Water	34.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	1.4
Total Parts	**100.00**

Preparation of a spray-dried laundry detergent powder.

An aqueous slurry having the composition as described above is prepared having a moisture content of 34.0%. Any ingredient added above in liquid form is heated to 70°C, such that the aqueous slurry is never at a temperature below 70°C. At the end of preparation, the aqueous slurry is heated to 80°C and pumped under pressure ($7.5x10^6$ Nm^{-2}), into a counter current spray-drying tower with an air inlet temperature of from between 250°C to 330°C. The in-let air fan is set such that the tower in-let air-flow is 187,500 kgh^{-1}. The exhaust air fan is controlled to give a negative pressure in the tower of -200 Nm^{-2} (typically the out-let air flow rate through the exhaust fan is between 220,000 kgh-1 to 240,000 kgh^{-1}, this includes the evaporated water from the slurry). The aqueous slurry is atomised and the atomised slurry is dried to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder, which is free-flowing. Fine material (<0.175mm) is elutriated with the exhaust the exhaust air in the spray-drying tower and collected in a post tower containment system. The spray-dried powder has a moisture content of 2.0wt%, a bulk density of 350g/l and a particle size distribution such that greater than 90wt% of the spray-dried powder has a particle size of from 175 to 710 micrometers. The temperature of the powder exiting the tower has a temperature of below 150°C. The composition of the spray-dried powder is given below.

Spray-dried laundry detergent powder composition.

Component	**%w/w Spray Dried Powder**
Linear alkyl benzene sulphonate	15.8
Acrylate/maleate copolymer	6.8
Ethylenediamine disuccinic acid and/or Hydroxyethane di(methylene phosphonic acid)	2.1
Sodium carbonate	28.7
Sodium sulphate	42.4

Water	2.0
Miscellaneous, such as magnesium sulphate, brightener, and one or more stabilizers	2.2
Total Parts	**100.00**

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

CLAIMS

What is claimed is:

1. A spray-drying process to prepare a spray-dried powder comprising:

(a) anionic detersive surfactant;

(b) from 0wt% to 10wt% zeolite builder;

(c) from 0wt% to 10wt% phosphate builder;

(d) optionally from 0wt% to 10wt% silicate salt;

(e) optionally carbonate salt;

(f) optionally polymeric material; and

(g) optionally from 0wt% to 10wt% water,

wherein, the process comprises the steps of:

(i) spraying an aqueous slurry comprising from

(a) anionic detersive surfactant;

(b) from 0wt% to 20wt% zeolite builder;

(c) from 0wt% to 20wt% phosphate builder;

(d) optionally from 0wt% to 20wt% silicate salt;

(e) optionally carbonate salt;

(f) optionally polymeric material; and

(g) water,

into a spray-drying zone, wherein the spray-drying zone is under negative pressure and wherein the air inlet air temperature into the spray-drying zone is greater than 150°C; and

(ii) drying the aqueous slurry to form a spray-dried powder.

2. A spray-drying process according to claim 1, wherein the spray-drying zone is under a pressure of at least -50Nm^{-2}.

3. A spray-drying process according to any preceding claim, wherein the spray-drying zone is under a pressure of at least -100Nm^{-2}.

4. A spray-drying process according any preceding claim, wherein the spray-drying zone is under a pressure of at least at least -200Nm^{-2}.

5. A spray-drying process according to any preceding claim, wherein the spray-dried powder comprises:

(a) from 0wt% to 2wt% zeolite builder;

(b) from 0wt% to 2wt% phosphate builder; and

(c) optionally, from 0wt% to 2wt% silicate salt.

6. A spray-drying process according to any preceding claim, wherein the spray-dried powder exiting the spray-drying zone has a temperature of less than 150°C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/026043

A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are includec in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 849 327 A (DISALVO W ET AL) 19 November 1974 (1974-11-19) column 3, line 35 - column 4, line 4 column 9, lines 65-69 claims; figure 1; examples	1-6
X	WO 01/44427 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]) 21 June 2001 (2001-06-21) page 4, line 11 - page 6, line 22; claims; examples	1-6
X	DE 42 08 773 A1 (COGNIS BIO UMWELT [DE]) 23 September 1993 (1993-09-23) page 3, lines 38-44; examples	1-6

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/026043

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3849327 A	19-11-1974	NONE	
WO 0144427 A1	21-06-2001	AU 1859501 A	25-06-2001
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		CN 1434854 A	06-08-2003
DE 4208773 A1	23-09-1993	NONE	

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(54) Title: PREPARATION OF SOLID CAPSULES COMPRISING FLAVOURS

(57) Abstract: The present invention relates to a process for the preparation of solid capsules comprising flavours, in which an emulsion comprising flavour or fragrance, a natural extract comprising saponins, water and a water-soluble biopolymer having a molecular weight below 100 KDa is spray-dried. The invention further relates to the solid capsules as such and to products containing them.

PREPARATION OF SOLID CAPSULES COMPRISING FLAVOURS

Technical Field

The present invention relates to a process for the preparation of solid capsules comprising flavours, in which an emulsion comprising flavour or fragrance, a natural extract comprising saponins, water and a water-soluble biopolymer having a molecular weight below 100 KDa is spray-dried. The invention further relates to the solid capsules as such and to products containing them.

Prior art

Spray-drying is a well known technique for the encapsulation of flavours. Spray-dried products are commonly prepared from an emulsion that is sprayed into a drying chamber. The emulsion typically comprises flavours, a carrier and an emulsifier.

A number of emulsion parameters influence the quality of the spray-dried solid capsules. In particular, it is well-known to the person skilled in the art of spray-drying that it is desirable to spray-dry a good emulsion, as defined by relatively small droplet size of the discontinuous phase, said emulsion also preferably remaining stable during the whole duration of the spray-drying process, taking into account that, depending on the manufacturing set up, the time-delay between emulsion preparation and actual spray-drying can vary from a few minutes to several hours. The stability of the droplet size in the emulsion is even more important and difficult to achieve when high amounts of flavours are intended to be encapsulated.

It is therefore desirable to provide solid capsules obtained from emulsions having an enhanced stability and in particular having a droplet size which remains stable during a prolonged period of time.

The nature of the spray-drying process also requires the emulsions to be sprayable. The emulsion therefore cannot exceed a certain viscosity limit, which depends on the apparatus used. In order to decrease the viscosity, it is known to add water to the emulsion. However, the additional water will have to be evaporated during the drying step. Such evaporation has a high energy cost. It would therefore be desirable to provide means to further reduce the viscosity of the sprayed emulsion without further increasing the proportion of water.

Most of the time, biopolymers with surface active properties, such as for example

gum arabic, modified starches, modified cellulose, gelatine, alginates or even proteins such as albumin or beta-globulin, are used as emulsifiers.

For example, US 2009/0253612 describes a spray-dry encapsulation process for flavour or fragrance comprising drying an aqueous emulsion containing the oil to be encapsulated, modified starch and phosphate salts.

Hidefumi et al., Innovative Food Science & Emerging Technologies, 2 (2001), pp. 55-61, discloses a process for the microencapsulation of emulsified ethyl butyrate by spray-drying using maltodextrin as carrier and gum arabic as emulsifier.

However, modified starch, modified cellulose, gelatine, alginates, proteins and especially gum arabic have undesired viscosifying properties. It would therefore be desirable to reduce the viscosity of such emulsions.

To solve this problem, it is already known to replace part of the gum arabic by low molecular weight emulsifiers such as fatty acids or glycerol esters. For example, WO 2006/082536 describes a method for the preparation of a spray-dried powder, which comprises the steps of emulsifying the active ingredient in a gum arabic and non-ionic emulsifier mixture, homogenizing the emulsion and spray-drying the latter to form a particulate product. The non-ionic emulsifiers may be a low molecular weight emulsifier such as di-acetyl tartaric acid esters of mono and diglycerides, such as DATEM or CITREM).

With the same concentrations of emulsifier, water and flavour, the viscosity of the emulsion is reduced when part of the biopolymer is replaced by such low molecular weight emulsifiers. However the major drawback of these low molecular weight emulsifiers is their tendency to stick to spray-drier chamber walls and to the surface of other particles in the spray-drier when they are used in sufficient amounts to reduce the viscosity of the emulsion.

It would therefore be desirable to provide a new encapsulation process, in which the viscosity of the sprayable emulsion is reduced compared to known sprayable emulsions having the same amount of solid, water and flavour, and in which the components of the sprayable emulsion have reduced tendency to stick to the drying chamber's walls.

In addition, due to the constantly growing consumers' request for natural products, it would be especially advantageous to provide a spray-dried product in which every component can be obtained from a natural source.

To the best of our knowledge none of the processes described in the prior art solves these problems.

Summary of the Invention

Accordingly, the invention relates to a process for preparing solid capsules, the process comprising the steps of :

a) preparing an emulsion comprising

i. from 0.1 to 10% of a natural extract comprising saponins;

ii. from 5 to 55% of a water soluble biopolymer having a molecular weight below 100 KDa;

iii. from 5 to 60% of flavour or fragrance; and

iv. from 15 to 80% of water;

the percentages being defined by weight, relative to the total weight of the emulsion;

b) spray-drying the emulsion obtained in step a) so as to obtain solid capsules.

In another aspect, the invention relates to solid capsules obtainable by the process of the invention.

In a further aspect the invention relates to a food product comprising the solid capsules of the invention.

Detailed description of the invention

The process of the present invention comprises the step of preparing an emulsion comprising

i. from 0.1 to 10% of a natural extract comprising saponins;

ii. from 5 to 55% of a water soluble biopolymer having a molecular weight below 100 KDa;

iii. from 5 to 60% of flavour or fragrance; and

iv. from 15 to 80% of water;

the percentages being defined by weight, relative to the total weight of the emulsion.

Saponins are amphiphilic glycosides composed of one or more hydrophilic glucoside moiety combined with a lipophilic triterpene derivative. Saponins are present in diverse plant extracts. As "natural extract comprising saponins" it is meant here any saponin or mixture of substances comprising saponins obtained by applying a physical separation process to a raw material that is available in nature. Preferred natural extracts

are those comprising at least 10% by weight, more preferably at least 20% by weight, even more preferably at least 50% by weight, most preferably at least 80% by weight, relative to the total weight of the extract, of saponins,

As preferred examples of natural extracts that can be used in the present invention, one can cite plant extracts, such as quillaja extract, camellia seeds extract, achyranthe extract, glycyrrhizine and stevia. Quillaja extract, which is obtained from the bark of *Quillaja saponaria* is particularly appreciated for the purpose of the present invention. Such plant extracts are commercially available from diverse suppliers. For example, quillaja extract can be purchased in a dilute form from National Starch under the trade name Q-Naturale™ (Quillaja extract in water).

In a preferred aspect of the invention, the extract is used in an amount of from 0.2 to 5% by weight, more preferably from 0.3 to 1% by weight, relative to the total weight of the emulsion.

Any water soluble biopolymer with a molecular weight below 100 KDa can be used for the purpose of the invention. By "water soluble biopolymer" is intended for the purpose of the present invention as any biopolymer which forms a clear solution in water, i.e. which forms a one-phase solution in water. Preferably, it forms a one phase solution when dissolved at 10%, more preferably even at 20% in water.

Preferred water soluble biopolymers are starch hydrolysates with a dextrose equivalent above 2. Examples of such biopolymers are di-saccharides, oligosaccharides, polysaccharides. Mostly preferred polysaccharides are selected from dextrins, maltodextrins and corn-syrup.

It is also particularly advantageous to use water soluble biopolymers which do not comprise any chemical substitution, meaning that the water soluble biopolymer has not been chemically (i.e. artificially) modified. Preferably, the water soluble biopolymer is available as such in nature and more preferably it is isolated from a natural source.

The water soluble biopolymer is preferably used in an amount of from 10 to 50% by weight, more preferably from 35 to 45% by weight, relative to the total weight of the emulsion.

For the purpose of the present invention, flavouring and/or perfuming ingredients encompass flavour and fragrance ingredients or compositions of current use in the flavour and/or fragrance industry, of both natural and synthetic origin. It includes single compounds and mixtures. Specific examples of such flavour and/or fragrance ingredients

may be found in the current literature, e.g. in Fenaroli's Handbook of flavour ingredients, 1975, CRC Press; Synthetic Food adjuncts, 1947 by M.B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander, 1969, Montclair, New Jersey (USA). Many other examples of current flavouring and/or perfuming ingredients may be found in the patent and general literature available. The flavouring and/or perfuming ingredients may be present in the form of a mixture with solvents, adjuvants, additives and/or other components, generally those of current use in the flavour and fragrance industry.

"Flavouring ingredients" are well known to a person skilled in the art of aromatising as being capable of imparting a flavour or taste to a consumer product, or of modifying the taste and/or flavour of said consumer product, or yet its texture or mouthfeel.

By "perfuming ingredients" it is understood here compounds which are used as active ingredients in perfuming preparations or compositions in order to impart a hedonic effect when applied on a surface. In other words, such compounds, to be considered as being perfuming ones, must be recognized by a person skilled in the art of perfumery as being able to impart or modify in a positive or pleasant way the odor of a composition or of an article or surface, and not just as having an odor. Moreover, this definition is also meant to include compounds that do not necessarily have an odor but are capable of modulating the odor of a perfuming composition, perfumed article or surface and, as a result, of modifying the perception by a user of the odor of such a composition, article or surface. It also contains malodor counteracting ingredients and compositions. By the term "malodor counteracting ingredient" we mean here compounds which are capable of reducing the perception of malodor, i.e. of an odor that is unpleasant or offensive to the human nose by counteracting and/or masking malodors. In a particular embodiment, these compounds have the ability to react with key compounds causing known malodors. The reactions result in reduction of the malodor materials' airborne levels and consequent reduction in the perception of the malodor.

There is no particular limitation as to the nature of the flavour and/or fragrance that can be encapsulated by the process of the present invention. However, flavours and/or fragrance characterized by a logP value of 2 or more are particularly preferred for the purpose of the present invention.

The flavour and/or fragrance is preferably used in an amount of from 7 to 30% by weight, more preferably from 10 to 15% by weight, relative to the total weight of the emulsion.

The emulsion may also contain optional ingredients. It may in particular further contain an effective amount of a fireproofing or explosion suppression agents. The type and concentration of such agents in spray-drying emulsions is known to the person skilled in the art. One can cite as non-limiting examples of such fireproofing or explosion suppression agents inorganic salts, C_1-C_{12} carboxylic acids, salts of C_1-C_{12} carboxylic acids and mixtures thereof. Preferred explosion suppression agents are, salicylic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, citric acid, succinic acid, hydroxysuccinic acid, maleic acid, fumaric acid, oxylic acid, glyoxylic acid, adipic acid, lactic acid, tartaric acid, ascorbic acid, the potassium, calcium and/or sodium slats of any of the afore-mentioned acids, and mixtures of any of these. Other optional ingredients include antioxidants, colorants and dyes.

The emulsion can be formed using any known emulsifying method, such as high shear mixing, sonication or homogenization. Such emulsifying methods are well known to the person skilled in the art.

The droplet size d(v,0.9) of the emulsion is preferably comprised between 1 and 15 µm, more preferably between 1 and 10 µm and even more preferably between 1 and 6 µm. More preferably, the droplet size remains within such range for at least one day storage at ambient temperature (25°C).

The viscosity of the emulsion is preferably comprised between 20 and 300 mPas, more preferably between 70 and 200 mPas and even more preferably between 100 and 150 mPas at the temperature at which the atomization step, as defined below, is carried out.

In step b), the emulsion is spray-dried so as to obtain solid capsules. The spray-drying process comprises two steps, the first one being dispersion and the second one being drying.

The emulsion is first subjected to an atomization step, during which the emulsion is dispersed in the form of drops into a spraying tower. Any device capable of dispersing the emulsion in the form of drops can be used to carry out such dispersion. For instance, the emulsion can be guided through a spraying nozzle or through a centrifugal wheel disk into the spraying tower. Vibrated orifices may also be used.

The size of the capsules is determined by the size of the drops that are dispersed into the tower. If a spraying nozzle is used for dispersing the drops the size may be controlled by the flow rate of an atomising gas through the nozzle, for example. In the case where a centrifugal wheel disk is used for dispersal, the main factor for adjusting droplet size is the centrifugal force with which the drops are dispersed from the disk into the tower. The centrifugal force, in turn, depends on the speed of rotation and the diameter of the disk. The feed flow rate of the emulsion, its surface tension and its viscosity are also parameters controlling the final drop size and size distribution. By adjusting these parameters, the skilled person can control the size of the drops of the emulsion to be dispersed in the tower.

Once sprayed in the chamber, the droplets are dried using any technique known in the art. These methods are perfectly documented in the patent and non-patent literature in the art of spray-drying. For example, Spray-Drying Handbook, 3rd ed., K. Masters; John Wiley (1979), describes a wide variety of spray-drying methods.

The process of the present invention may be performed in any conventional spraying tower. A conventional multi-stage drying apparatus is for example appropriate for conducting the steps of this process. It may comprise a spraying tower, and, at the bottom of the tower, a fluidised bed intercepting partially dried particles after falling through the tower.

The solid capsules obtainable and/or obtained by the process described above are also an object of the present invention.

The obtained solid capsules typically comprise

- from 0.5 to 30% of a natural extract comprising saponins
- from 15 to 94% of a water soluble biopolymer having a molecular weight below 100 KDa,
- from 5 to 75% of flavour or fragrance; and
- from 0.5 to 10% of water;

the percentage being defined by weight, relative to the total weight of the capsules.

All components of the capsules are as defined above.

Preferably the solid capsules comprise between 0.5 and 5% by weight, preferably between 0.5 and 3% by weight of water, relative to the total weight of the solid capsules.

In a preferred aspect of the invention the size of the particles is typically comprised between 20 and 200 µm, more preferably between 50 and 100 µm, even more preferably from 75 to 85 µm.

The capsules of the invention have satisfying storage stability, even at 60% relative humidity.

In another aspect, the invention relates to a food product comprising the solid capsules of the invention. The food product of the invention preferably is a particulate or powdery food. In such a case, the capsules of the invention may easily be added thereto by dry-mixing.

In a preferred aspect of the invention, the food product is selected from the group consisting of an instant soup or sauce, a breakfast cereal, a powdered milk, a baby food, a powdered drink, a powdered chocolate drink, a spread, a powdered cereal drink, a chewing gum, an effervescent tablet, a cereal bar, and a chocolate bar. The powdered foods or drinks may be intended to be consumed after reconstitution of the product with water, milk and/or a juice, or another aqueous liquid.

Examples

The invention will now be described in further detail by way of the following examples.

Example 1

Preparation of solid capsules according to the invention

Emulsion A was prepared by homogenizing the following ingredients:

Table 1 : Composition of Emulsion A

Ingredient	Parts [%]
Natural extract comprising saponins[1)]	5
Polysaccharide[2)]	38.6
Flavour[3)]	14.3
Water	42.1

1) Q-Naturale™ (Solution of quillaja extract in water, origin: National Starch)
2) Glucidex® 18 DE (Maltodextrin, origin: Roquette Frères)
3) Limonene

The emulsion had a viscosity of 113 mPas at 25°C and the droplet size d(v,0.9) was of 1.8 µm.

Capsules A were prepared by spray-drying Emulsion A using a Buchi Mini Spray-Dryer B-290, supplied by Büchi, Flawil, Switzerland, with an air inlet temperature set to 180°C. The air outlet temperature was of 100°C. The emulsion before atomization was at ambient temperature.

The obtained capsules had the following composition:

Table 2 : Composition of Capsules A

Ingredient	Parts [%]
Natural extract comprising saponins[1)]	1.6
Polysaccharide[2)]	79.4
Flavour[3)]	16.4
Water	2.6

1) Dry quillaja extract
2) Glucidex® 18 DE (Maltodextrin, origin: Roquette Frères)
3) Limonene

The obtained capsules were characterized by a glass transition temperature of 85°C and the particle size d(v,0.9) was 78 µm.

Example 2

Preparation of solid capsules according to the invention

Emulsion B was prepared by homogenizing the following ingredients:

Table 3 : Composition of Emulsion B

Ingredient	Parts [%]
Natural extract comprising saponins[1)]	2
Polysaccharide[2)]	41.2
Flavour[3)]	14.3
Water	42.5

1) Q-Naturale™ (Solution of quillaja extract in water, origin: National Starch)
2) Glucidex® 18 DE (Maltodextrin, origin: Roquette Frères)
3) Limonene

The emulsion had a viscosity of 130 mPas at 25°C and the droplet size d(v,0.9) was of 5.4 µm.

Capsules B were prepared by spray-drying Emulsion B using a Buchi Mini Spray-Dryer B-290, supplied by Büchi, Flawil, Switzerland, with an air inlet temperature set to 180°C. The air outlet temperature was of 100°C. The emulsion before atomization was at ambient temperature.

The obtained capsules had the following composition:

Table 4 : Composition of Capsules B

Ingredient	Parts [%]
Natural extract comprising saponins[1)]	0.6
Polysaccharide[2)]	80.8
Flavour[3)]	16.6
Water	2.0

1) Dry quillaja extract
2) Glucidex® 18 DE (Maltodextrin, origin: Roquette Frères)
3) Limonene

The obtained capsules were characterized by a glass transition temperature of 90°C and the particle size d(v,0.9) was 80 µm.

Claims

1. A process for preparing solid capsules, the process comprising the steps of:

a) preparing an emulsion comprising

- from 0.1 to 10% of a natural extract comprising saponins;
- from 5 to 55% of a water soluble biopolymer having a molecular weight below 100 KDa;
- from 5 to 60% of flavour or fragrance; and
- from 15 to 80 % of water;

the percentages being defined by weight, relative to the total weigh of the emulsion;

b) spray-drying the emulsion obtained in step a) so as to obtain solid capsules.

2. A process according to claim 1 , wherein the natural extract comprises at least 10% by weight of saponins, relative to the total weight of the extract.

3. A process according to claim 1 or 2, wherein the natural extract is a plant extract.

4. A process according to claim 3, wherein the natural extract is a quillaja extract.

5. A process according to any one of claims 1 to 4, wherein the water soluble biopolymer is a starch hydrolysate with a dextrose equivalent above 2.

6. A process according to any one of claims 1 to 4, wherein the water soluble biopolymer is a selected from dextrins, maltodextrins and corn syrup.

7. A process according to any one of claims 1 to 6, wherein the flavour or fragrance has a logP value of 2 or more.

8. A process according to any one of claims 1 to 7, wherein the natural extract is used in an amount comprised between 0.2 and 5% by weight, relative to the total weight of the emulsion.

9. A process according to any one of claims 1 to 8, wherein the water soluble polymer is used in an amount comprised between 10 and 50% by weight, relative to the total weight of the emulsion.

10. A process according to any one of claims 1 to 9, wherein the flavour or fragrance is used in an amount comprised between 7 and 30% by weight, relative to the total weight of the emulsion.

11. Solid capsules obtainable by the process of any one of claims 1 to 10.

12. Solid capsules according to claim 11, comprising:

- from 0.7 to 30% of a natural extract comprising saponins
- from 15 to 95% of a a water soluble biopolymer having a molecular weight below 100 KDa,
- from 5 to 75% of flavour; and
- from 0.5 to 10% of water;

the percentages being defined by weight, relative to the total weight of the capsules.

13. A food product comprising the solid capsules according to claim 11 or 12.

14. A food product according to claim 13, in the form of a particulate or powdery food.

15. A food product according to claim 13 or 14, in the form of an instant soup or sauce, a breakfast cereal, a powdered milk, a baby food, a powdered drink, a powdered chocolate drink, a spread, a powdered cereal drink, a chewing gum, an effervescent tablet, a cereal bar, and a chocolate bar.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/050975

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/00 A23L1/035 A23L1/09 A23L1/22 A23P1/04
B01J13/02 B01J13/04
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, BIOSIS, FSTA, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 482 433 B1 (DEROOS KRIS BART [CH] ET AL) 19 November 2002 (2002-11-19) column 5, line 30 - column 6, line 15; examples 1,2 column 6, line 38 - line 49	1-15
A	EP 1 252 828 A2 (TAKASAGO PERFUMERY CO LTD [JP]) 30 October 2002 (2002-10-30) paragraph [0018]	1-15
A	US 2006/222766 A1 (MUELLER ROLF [CH] ET AL) 5 October 2006 (2006-10-05) claims 28-31	1-15
A	US 6 576 247 B1 (IKEMOTO TAKESHI [JP] ET AL) 10 June 2003 (2003-06-10) column 6, line 8 - line 30	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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(54) Title: SPRAY-DRIED COMPOSITIONS CAPABLE OF RETAINING VOLATILE COMPOUNDS AND METHODS OF PRODUCING THE SAME

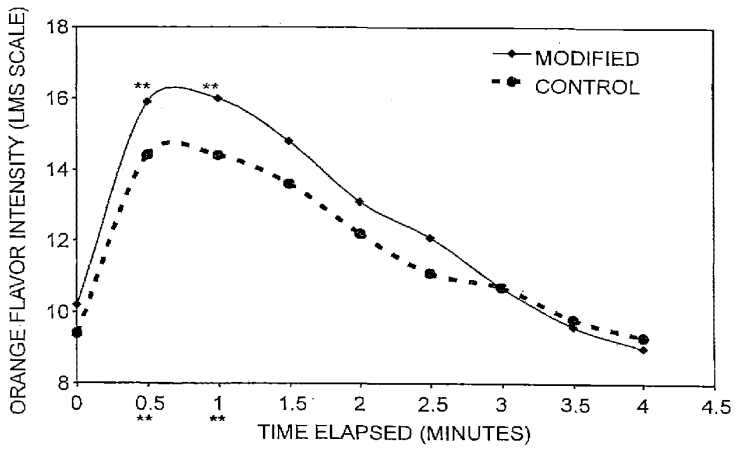


FIG. 2

(57) Abstract: The present invention relates to spray-dried compositions capable of retaining volatile compounds and methods relating to the same. The present invention also relates to the powders produced by such methods.

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IFF0049WO PATENT

SPRAY-DRIED COMPOSITIONS CAPABLE OF RETAINING VOLATILE COMPOUNDS AND METHODS OF PRODUCING THE SAME

Introduction

[0001] This patent application claims the benefit of priority from U.S. Provisional Application Serial Number 61/449,440, filed March 4, 2011, the content of which is herein incorporated by reference in its entirety.

Background of the Invention

[0002] In the food industry, spray drying, freeze-drying, vacuum continuous belt drying, and reduced pressure-low temperature drying with a vacuum dryer have been used to produce dry powders of flavor ingredients such as, for example, dry extracts of animals and plants.

[0003] Spray drying is a common industrial method for drying liquid solutions or slurries by spraying into a stream of hot gas. It is a rapid, one-step process for converting the feed liquid into a powder. Usually the drying gas is air, but nitrogen can also be used for special products needing oxygen-free conditions. The most common feed materials are aqueous-based solutions, emulsions and suspensions, where water is evaporated in the dryer. The liquid feed is fed to an atomizer, which is a device that breaks up the liquid stream into tiny droplets. This atomization takes place within the drying chamber so that the droplets are immediately exposed to hot air that initiates rapid moisture evaporation. The droplets become small particles of powder as the moisture is evaporated and they fall to the bottom of the drying chamber. Pressure nozzles, rotary disks, two-fluid nozzles, and the like are used as the atomizing unit. In many cases, the mean particle size (diameter) of the resulting dry powder is

about 20 μm to 500 μm, and the drying time is as short as 5 to 30 seconds (see, Handbook of Chemistry and Engineering (1999) revised sixth edition, Maruzen Corporation, p. 770, p. 780). A four-fluid nozzle has also been developed, which has enabled mass-scale spray drying with a liquid droplet having a mean particle size of several micrometers.

[0004] The spray drying method is used in many cases of mass scale production. In general, to produce a large volume of powder in a short period of time, a solution or slurry is fed at a fast feed rate into a spray dryer, while the inlet temperature of the spray dryer and the outlet temperature thereof are elevated as high as possible, to dry the slurry at a high speed. For example, milk is dried at an inlet temperature of the spray dryer of 150 to 250°C and yeast is dried at the inlet temperature of 300 to 350°C. Drying at such high temperatures may negatively impact the flavor of the raw material itself and produce a dry powder with a burned odor. However, spray drying at a low temperature to avoid these disadvantages can increase process times and costs. See US 2005/0031769 and US Patent No. 6,482,433.

[0005] Spray-dried encapsulated flavors are created during the drying process when the aqueous carrier slurry forms a shell around the normally oil-based flavor core. During the drying process, a thin film of carrier material rapidly forms around the atomized droplet and selectively allows water to evaporate while retaining the flavor oil (Thijssen & Rulkens (1968) *De Ingenieur* 80:45-56). The shell protects the core against deterioration and volatile evaporation, but also allows the core to be released under desired conditions, for example, dissolution in water.

[0006] There has been a long felt need to spray dry natural and synthetic materials to provide intense fresh, authentic

consumer preferred flavors in foodstuffs and other flavor-containing products. Likewise, there is a similar need to spray dry natural and synthetic materials to provide intense, fresh, authentic consumer preferred fragrances in consumer products.

Summary of the Invention

[0007] The present invention is a spray-dried flavor composition containing a spray-dried flavor that has volatile compounds, wherein the volatile compounds are present in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

[0008] The invention also provides a spray-dried flavor composition produced by spray drying a flavor that contains volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

[0009] The invention also provides a stable spray-dried flavor composition produced by spray drying a flavor that that contains volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

[0010] A method for producing a spray-dried composition capable of retaining volatile compounds is also embraced by the present invention. In accordance with this method, a flavor containing volatile compounds is spray dried in a spray dryer having an inlet temperature of less than 100°C

and an air inlet dew point -10°C to 5°C to obtain a spray-dried flavor composition, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

[0011] In accordance with certain embodiments of the composition and methods of this invention, the spray-dried composition may be subjected to an additional drying step in a fluid-bed chamber attached at the spray dryer outlet, wherein the temperature of the air of the fluid-bed unit is at or below the outlet temperature of the spray dryer. In other embodiments, the volatile compounds are acetaldehydes, dimethyl sulfides, ethyl acetates, ethyl propionates, methyl butyrates, or ethyl butyrates. In yet other embodiments, the volatile compounds have a boiling point of less than 200°C, less than 100°C, or less than 60°C.

[0012] In further embodiments, the composition fed to the dryer may further include a carrier material and/or a solvent, such as a volatile solvent, wherein the flavor and carrier comprise 40% and 70% as dry solid material of the total composition. For the purpose of the invention, a dry solid material is defined as a combination of carrier and flavor materials. In yet other embodiments, the flavor is prepared as an emulsion and the volatile compounds are present in the emulsion in an amount that is at least 80% of the volatile compounds originally contained in the flavor. Still further embodiments include the use of nitrogen or carbon dioxide in the spray dryer. In certain embodiments, the air inlet temperature is in the range of 40°C to 99°C. Flavor compositions with a water activity in the range of 0.1 to 0.6 and high intensity flavor

compositions and their use in, *e.g.*, a chewing gum or beverage are also provided.

Brief Description of the Drawings

[0013] Figure 1 shows a comparison of sensory profiles of Orange Flavor between samples produced under different RH/Temperature conditions in a beverage tasting solution. *Directionally different, **Significantly different at p=0.05

[0014] Figure 2 shows a comparison of time intensity profiles of Orange Flavor between samples produced under different humidity/temperature conditions in sugar-free chewing gum. **Significantly different at p=0.05 at these elapsed times.

[0015] Figure 3 shows a comparison of sensory profiles of Berry Flavor between samples produced under different humidity/temperature conditions in a beverage tasting solution. ** Significantly different at p = 0.05.

[0016] Figure 4 shows a comparison of time intensity profiles of Berry Flavor between samples produced under different humidity/temperature conditions in sugar-free chewing gum. **Significantly different at p=0.05 at these elapsed times.

[0017] Figure 5 is a diagram of dryer airflow used in the production of the instant composition.

Detailed Description of the Invention

[0018] It has been found that commercially available spray dryer nozzles, geometries, and circulation patterns can be used in methods of producing powders with high volatile retention and high flavor intensity, even when drying for an extended amount of time. In particular, when a conventional spray dryer is used with an inlet temperature

of less than 100°C and a dew point -10°C to 5°C, higher levels of volatile compounds can be retained. Because of the increased efficiency of the method described herein, drying of flavor compositions containing volatile compounds can be achieved at relatively low temperatures compared to conventionally used methods. The resulting spray-dried flavor composition has high intensity flavor and has a high flavor/fragrance quality that is authentic to the natural source. Surprisingly, these flavor compositions maintain high flavor intensity and flavor/fragrance quality in various end-use applications after long-term storage.

[0019] The invention also provides a stable spray-dried flavor composition produced by spray drying a flavor that that contains volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor. For the purpose of this invention stability is defined as a flavor quality and intensity that remains acceptable for use in end use applications. Preferably, a stable spray-dried flavor composition has a shelf-life of up to three years depending on storage conditions. Consumer data, as demonstrated in the examples herein, showed statistically significant preference for the flavors composition of the present invention. The consumer preferred quality of the flavor composition is further supported by the attributes selected by consumers to describe the flavor quality of the prototypes.

[0020] Therefore, the present invention is a spray-dried flavor composition and a method for producing such a composition. In accordance with the present invention, a spray-dried flavor composition containing one or more

volatile compounds is produced by spray drying a flavor in a spray dryer with an inlet temperature of less than 100°C and a dew point -10°C to 5°C so that a dry powder is obtained. In certain embodiments, the resulting spray-dried composition is further dried in a fluidized bed. As a result of the instant method, the spray-dried flavor composition retains at least 20% of the volatile compounds originally contained in the flavor.

[0021] Unless otherwise specified, a flavor of the invention is a flavor that contains one or more volatile compounds. A variety of flavors can be used in accordance with the present invention. Flavor may be chosen from synthetic flavor and flavoring aromatics, and/or oils, oleo resins and oil extracts derived from plants, leaves, flowers, fruits, and combinations thereof. Representative flavor oils include, but are not limited to, spearmint oil, cinnamon oil, peppermint oil, clove oil, bay oil, thyme oil, cedar leaf oil, oil of nutmeg, oil of sage, and oil of bitter almonds. Also useful are artificial, natural or synthetic fruit flavors such as vanilla, chocolate, coffee, cocoa and citrus oil, including lemon, orange, grape, lime and grapefruit, and fruit essences including apple, pear, peach, strawberry, raspberry, cherry, plum, pineapple, apricot and so forth. These flavors can be used individually or in admixture.

[0022] The volatile compounds of the instant flavor may include, but are not limited to, acetaldehyde, dimethyl sulfide, ethyl acetate, ethyl propionate, methyl butyrate, and ethyl butyrate. Flavors containing volatile aldehydes or esters include, *e.g.*, cinnamyl acetate, cinnamaldehyde, citral, diethylacetal, dihydrocarvyl acetate, eugenyl formate, and p-methylanisole. Further examples of volatile compounds that may be present in the instant flavor oils

include acetaldehyde (apple); benzaldehyde (cherry, almond); cinnamic aldehyde (cinnamon); citral, *i.e.*, alpha citral (lemon, lime); neral, *i.e.*, beta citral (lemon, lime); decanal (orange, lemon); ethyl vanillin (vanilla, cream); heliotropine, *i.e.*, piperonal (vanilla, cream); vanillin (vanilla, cream); alpha-amyl cinnamaldehyde (spicy fruity flavors); butyraldehyde (butter, cheese); valeraldehyde (butter, cheese); citronellal (modifies, many types); decanal (citrus fruits); aldehyde C-8 (citrus fruits); aldehyde C-9 (citrus fruits); aldehyde C-12 (citrus fruits); 2-ethyl butyraldehyde (berry fruits); hexenal, *i.e.*, trans-2 (berry fruits); tolyl aldehyde (cherry, almond); veratraldehyde (vanilla); 2,6-dimethyl-5-heptenal, *i.e.*, melonal (melon); 2-6-dimethyloctanal (green fruit); and 2-dodecenal (citrus, mandarin); cherry; or grape and mixtures thereof. The composition may also contain taste modulators and artificial sweeteners.

[0023] The physical, chemical, and odor properties of selected volatile compounds are presented in Table 1.

TABLE 1

Compound	MW (g/mol)	Boiling Point (°C)	Water Solubility (g/L, approx.)	Odor Descriptors*
acetaldehyde	44.05	21	soluble	pungent; ethereal
dimethyl sulfide	62.02	36	insoluble	cabbage
ethyl acetate	88.11	77	90	ethereal; fruity
ethyl propionate	102.13	99	14	sweet; fruity; ethereal
methyl butyrate	102.13	102	15	fruity; pineapple
ethyl butyrate	116.16	121	6	fruity; pineapple

* The Good Scents Company and Merck Index, 12th Ed.

[0024] The instant invention is particularly useful in processing flavors with volatile compounds having a boiling point of less than 200°C, less than 150°C, less than 120°C, less than 100°C, less than 80°C, less than 60°C, less than 40°C, less than 20°C, or less than 0°C. Using such flavors, higher levels of volatile compounds are retained, which results in a sensory perceivable difference over conventional drying processes.

[0025] In certain embodiments, the invention further includes the use of a carrier material to enhance processing productivity and flavor intensity. Such carriers can include any sugar, sugar derivatives, modified starch, proteins, celluloses, salts, dextrins, gums, sugar alcohols, polyols, peptides, acids, carbohydrates or hydrocolloids. Particular examples of suitable materials include sugars such as sucrose, glucose, lactose, levulose, trehalose, fructose, maltose, ribose, dextrose, isomalt, sorbitol, mannitol, xylitol, lactitol, maltitol, pentatol, arabinose, pentose, xylose, galactose; hydrogenated starch hydrolysates; maltodextrins or dextrins (soluble fiber); hydrocolloids such as agar or carrageenan; gums; polydextrose; proteins such as soy and whey protein isolates and hydrolyzates, and sodium caseinates; and derivatives and mixtures thereof. The carrier can be selected based upon, amongst other factors, the desired flavor, authentic taste and intensity to be achieved.

[0026] In some embodiments, the flavor and optional carrier material are dissolved or emulsified in a solvent and subsequently spray-dried. In some embodiments, the solvent is water. In other embodiments, the solvent is not water. In yet further embodiments, the solvent is a volatile solvent. In still other embodiments, the solvent is a

mixture of water and a volatile solvent. As is known in the art, a volatile solvent is a nonaqueous liquid with solvent properties with the characteristic of evaporating readily at room temperature and atmospheric pressure. Volatile solvents of particular use in accordance with the present invention include, but are not limited to, ethanol, ethyl acetate, acetone.

[0027] Flavor emulsions can be prepared according to standard preparation procedures. Briefly, the practice involves dispersing and dissolving the dry carrier materials in solvent until free of lumps. When using water as the solvent, it may be desirable to warm the water (*e.g.*, to approximately 50°C) prior to adding the carrier material. The flavor is then added under constant agitation until a homogeneous mixture is obtained. The emulsion may be further subjected to high shear or homogenized to reduce oil droplet size prior to spray drying.

[0028] In certain embodiments, the emulsion contains between 40% and 70% dry solid material (including the flavor), or more preferably between 55% and 65% dry solid material (including the flavor). The amount of dry solid material can be adjusted by using more or less water depending on the solubility of the carrier material and various factors related to efficient operation of the spray dryer. For example, the type and amount of carrier, amount of water, and/or amount of flavor can be adjusted so that the resulting emulsion has a viscosity suitable for feeding into a spray dryer to provide liquid droplets having a mean particle size (mean volume diameter) of between 10 μm and 200 μm. For example, when using spray nozzles, such as a three-fluid nozzle and a four-fluid nozzle, the viscosity of the feed slurry is preferably 500 cps or less, preferably 200 cps or less, and more preferably 80 cps or

less. For a rotary atomizer (rotary disk), the viscosity is preferably 70,000 cps or less. Moreover, the feed slurry (*i.e.*, emulsion) can be heated (*e.g.*, to near the inlet temperature) or cooled (*e.g.*, to 15°C) immediately before adding it to the spray dryer to modify fluidity. In addition, certain flavors, especially those that are more water-soluble, act as plasticizers thereby making processing more difficult due to stickiness. In this respect, the ratios of carrier materials can be modified. Therefore, various factors can be appropriately selected or modified for use in combination with different spray dry apparatuses.

[0029] In addition to the flavor and carrier material, an emulsifier or surfactant can also be used in the production of the instant spray-dried flavor composition. Examples of suitable emulsifiers or surfactants include, but are not limited to, lecithins, sucrose esters, proteins, gums, soap-bark extract, saponins, and the like. Moreover, a variety of solvents can be used in the instant spray-dried flavor composition. Such solvents include, volatiles and nonvolatiles but are not limited to alcohol (*e.g.*, ethanol), ethyl acetate, acetone, triglycerides, vegetable oils, animal fats, and triacetin.

[0030] Commercially available spray dryers can be used as in the practice of the present invention. For example, a spray dryer with a vertical parallel flow function can be used. The spray dryer should be a system with a dehumidifying and drying function. For example, a spray dryer capable of blowing a high volume of desiccated air with a dew point of less than 5°C is particularly preferable. For a spray dryer with no dehumidifying and drying function, the spray dryer is inevitably arranged with a dry dehumidifier, *e.g.*, a honeycomb-type rotary

dehumidifier *(e.g.,* Nichias Corporation or Sweden PROFLUTE Corporation). Suitable spray dryers include the micromist spray dryer and the hybrid granulator series manufactured by Fujisaki Electric Co., Ltd.; the fluidized spray dryer FSD with internal fluid bed as manufactured by Niro Corporation; the fluid granulation spray dryer and L-8 type spray dryer manufactured by Ogawara (Japan); the DL-21 type and GB-21 type spray dryers manufactured by Yamato Scientific Co., Ltd., and Anhydro Spray Bed Dryer manufactured by SPX Corporation.

[0031] In particular embodiments, the spray dryer is capable of generating liquid droplets (particles) having a mean particle size (mean volume diameter) of between about 10 μm to about 200 μm. Specifically, it is preferred to carry out spray drying with a spray dryer with a spray nozzle capable of generating a large volume of liquid droplets having a mean particle size of between about 10 μm to about 200 μm, preferably about 20 μm to about 150 μm, and more preferably about 30 μm to about 100 μm. When the liquid droplets are dried, a dry powder having a mean particle size (mean volume diameter) of about 10 μm to about 100 μm is preferred for retention of the flavor oil.

[0032] Among the operation conditions of the spray drying apparatus, in certain embodiments the outlet temperature of the spray drying apparatus is between 20°C and 60°C, preferably 30 to 60°C, and more preferably 40 to 60°C. For the purposes of this invention, the outlet temperature of the spray dryer means the product temperature of the dry powder in the vicinity of the powder collection part of the spray dryer. For the spray dryer of the vertical parallel flow type, the outlet temperature means the temperature (exhaust gas temperature) at the exhaust part thereof.

[0033] In other embodiments of this invention, the average inlet air temperature of the spray drying apparatus is less than 100°C. In certain embodiments, the average inlet air temperature of the spray drying apparatus is in the range of 40°C to 99°C, more preferably 60°C to 99°C and most preferably 80°C to 99°C. For the purposes herein, the average inlet air temperature is a sum total of all inlet air streams, *e.g.*, main chamber inlet air and the inlet air to the fluid bed(s).

[0034] As a particular feature of the instant invention, it is desirable that production parameters including temperature, pressure and humidity, are controlled to achieve an air inlet dew point in the range of -10°C to 5°C. In particular embodiments, the air inlet dew point of the spray drying apparatus is 5°C or less, preferably 0°C or less, more preferably is -5°C or less, and most preferably -7.5°C or less. As is known in the art, dew point temperature is a function of air temperature and %RH and can be determined using a psychrometric chart or calculator. Dew point temperature is important as it corresponds directly to the actual amount of water in the air on a mass basis.

[0035] Once the spray-dried flavor composition is dried or partially dried in the spray drier, the resulting powder can be used in the production of food product, pharmaceuticals, consumer products and the like. Alternatively, particular embodiments feature the additional step of further drying the spray-dried flavor composition in a fluid-bed chamber attached at the outlet of the spray dryer. Accordingly, certain embodiments feature the use of an integrated fluid-bed spray dryer to produce the instant spray-dried flavor composition. This secondary drying can, *e.g.*, further remove entrapped

solvent, residual moisture, and/or water of molecular hydration, to provide a composition of powder particles with significantly lower moisture content that is stable in storage, *e.g.*, for extended periods at ambient temperatures.

[0036] In accordance with this embodiment, the temperature of the air supplying the fluid-bed unit is maintained at or below the outlet temperature of the spray dryer in order to maintain the benefit of volatile flavor retention. Thus, the inlet temperature of the fluid-bed unit is between 40°C and 99°C, preferably 50 to 95°C, and more preferably 60 to 90°C; and the inlet dew point is in the range of -10 to 5°C.

[0037] In some embodiments, the fluid-bed has a single zone. In other embodiments, the fluid-bed unit has one, two, three or more zones, wherein each zone has a different temperature and air flow rate. In certain embodiments, the fluid-bed unit has three zones, each varying in temperature by at least 10°C. In particular embodiments, the fluid-bed unit has three zones, each varying in temperature by 10°C to 20°C. By way of illustration, dry powder from a spray dryer with an outlet temperature of 60°C could have a first fluid-bed zone at 60°C, a second bed zone of 45°C and a third zone of 25°C.

[0038] Secondary drying can continue, *e.g.*, for about 5 minutes to about 5 hours, or about 10 minutes to about 1 hour, and most preferably about 20 to 40 minutes until residual moisture is reduced to a desired level. In particular embodiments, secondary drying continues until the residual moisture of the powder particles is below 5 percent.

[0039] As used herein, "dry," "dried," and "substantially dried" encompass those compositions with from about 0% to

about 15% water. Preferably, the instant composition will have a water activity of 0.1 to 0.6, or more desirably 0.2 to 0.5, and most preferably from 0.2 to 0.4 wherein said levels of dryness can be achieved with or without secondary drying.

[0040] Drying can also occur in the total or partial absence of ambient air. In this respect, drying can occur in the presence of CO_2 or other drying gases (*e.g.*, nitrogen). Accordingly, in particular embodiments, the air of the spray dryer is partially or wholly composed of carbon dioxide or nitrogen. In accordance with this embodiment, partial carbon dioxide or nitrogen is intended to mean a level in the range of 80-99% carbon dioxide and/or nitrogen.

[0041] Once the spray-dried flavor composition reaches the desired level of dryness, it can be used in a variety of consumer, food, or pharmaceutical products. In particular, the instant spray-dried flavor composition finds application in gums, confections, oral care products, beverages, snacks, dairy products, soups, sauces, condiments, detergents, fabric softeners and other fabric care products, antiperspirants, deodorants, talc, kitty litter, hair care and styling products, personal care products, air fresheners, cereals, baked goods and cleaners. In specific embodiments, the instant spray-dried flavor composition is used in flavoring chewing gum and beverages. Additionally, the spray-dried powder may be further processed by extrusion, coating, agglomeration, blending, compaction to impart additional functionality or benefits. While the instant invention is described in terms of the spray drying technique, the instant invention can employ other drying technologies or processes wherein the

use of low humidity and temperature conditions result in improved product quality through volatile retention.

[0042] Other modifications of this invention will be readily apparent to those skilled in the art. Such modifications are understood to be within the scope of this invention. As used herein, all percentages are weight percent unless otherwise noted, L is understood to be liter, kg is understood to be kilogram, and g to be gram. In addition, the amounts, sizes, temperatures and percentages provided herein are understood to include exact numbers and approximations.

[0043] The following examples are provided as specific embodiments of the present invention.

Example 1: Formulations for Dry Flavor Powders

[0044] A comparison between modified formulas and conventional control formulas was conducted. Exemplary Control and Modified formulas of dry flavor powders are listed in Table 2.

TABLE 2

Component	Control	Modified	Control	Modified
Orange Flavor	20%	16%		
Berry Flavor			11%	16%
Modified starch	10%	8%	72%	8%
Carbohydrates (*e.g.*, sugar, corn syrup, maltodextrin)	70%	76%	17%	76%

[0045] Control powders were produced by a conventional process conditions and Modified powders were produced by the instant modified process (Figure 5), according to the conditions listed in Table 3. In both cases, a conventional spray dryer without an integrated fluid-bed was used.

TABLE 3

Spray Dryer Operating Parameter	Standard	Modified
Inlet air temperature (°C)	170 - 210	< 100
Inlet air humidity (g H_2O/kg dry air)	2 - 18	0 - 4
Outlet air temperature (°C)	80 - 100	35 - 55
Outlet air humidity (g H_2O/kg dry air)	45 - 55	10 - 20
Atomizer type	Rotary Disc	Rotary Disc or Nozzle

[0046] All formulations ran well with minimal hold-up, sticking, or other issues in the conventional spray dryer.

Example 2: Retention of Volatile Compounds in Modified Orange Flavor Formulation

[0047] Using GC-FID (gas chromatography-flame ionization detector) analysis, the volatile profile of the Orange Flavor formulations in Example 1 was determined. This analysis indicated that the retention of specific volatile materials for the Modified powder compared to the level in the emulsion were approximately 72%, 75%, and 52% for ethyl propionate, ethyl butyrate, and acetaldehyde, respectively. Table 4 indicated the ratio of volatiles retained in the Modified powder in comparison to the Control powder. Sensory tests showed benefit of the Modified powder over the Control powder in a beverage tasting solution (significantly greater overall aroma and orange flavor; Figure 1) and in chewing gum (significantly greater orange flavor intensity at the 30 and 60 second intervals; Figure 2).

TABLE 4

Orange Flavor	Ethyl Propionate	Ethyl Butyrate	Acetaldehyde
Modified	2.3	1.6	1.8
Control	1.0	1.0	1.0

Example 3: Retention of Volatile Compounds in Modified Berry Flavor Formulation

[0048] Using GC-FID analysis, the volatile profile of the Berry Flavor formulations in Example 1 was determined. This analysis indicated that the retention of specific volatile materials for the Modified powder compared to the level in the emulsion were approximately 24%, 35%, and 87% for dimethyl sulfide, ethyl acetate, and ethyl butyrate, respectively. Table 5 indicated the ratio of volatiles retained in the modified powder in comparison to the Control powder. Sensory tests showed benefit of the Modified powder over the Control powder in a beverage tasting solution (significantly greater berry aroma and flavor, among others; Figure 3) and in chewing gum (significantly greater berry flavor intensity at the 30 and 60 second intervals; Figure 4).

TABLE 5

Berry Flavor	Dimethyl Sulfide	Ethyl Acetate	Ethyl Butyrate
Modified	12.7	13.4	4.5
Control	1.0	1.0	1.0

Example 4: Effects of Dryer Process Temperatures

[0049] To determine the effect of dryer process temperatures on the physical properties and flavor quality of a citrus flavor, different spray dryer air inlet and outlet temperatures were utilized. The resulting volatile

compound content, and flavor strength and aroma as determined by an expert panel are presented in Table 6.

TABLE 6

Inlet/Outlet Temperature (°C)	Water activity	Acetaldehyde Content (% of Nominal)	Flavor Strength Ranking	Aroma Strength Ranking
190/90	0.16	37	1	1
93/45	0.27	42	2*	2*

*2 = higher.

[0050] In addition to the above results, both spray-dried compositions exhibited free-flowing properties after 7 weeks at 40°C in a closed container. These results indicate that an air inlet temperature below 100°C reduces loss of volatile flavor compounds, provides improved sensory intensity, while maintaining water activity of the product at a level that prevents caking when exposed to above ambient temperatures.

Example 5: Stability of Fruit and Mint Flavors in Chewing Gum

[0051] The stability of apple and mint flavors in chewing gum were evaluated. Flavor compositions were spray-dried in accordance with the instant method, incorporated into chewing gum, and the stability of the flavor was evaluated by an expert panel after storage at 32°C for 2 or 12 weeks or 21°C for 12 weeks. The results of prototype apple-flavored gum, as compared to a control, are presented in Table 7 and Figure 6. The control samples were spray dried flavors processed using conventional drying conditions.

TABLE 7

Apple Flavored Gum	Prototype Flavor Stability			Control Flavor Stability		
	32°C		21°C	32°C		21°C
	2 weeks	12 weeks	12 weeks	2 weeks	12 weeks	12 weeks
Candy Banana	4.5	4.5	4	4	2	3
Green Apple	5.5	4	4.5	3	2	3
Ripe Estery	6	5	5.5	4	3	4
Sweet	n.d.	6	6	n.d.	5	5
Sour	n.d.	4	4	n.d.	3	3.5
Salivating	n.d.	4	5	n.d.	3	4
Astringent	n.d.	3	3	n.d.	2.5	3

Scale: 10-point scale (10=highest). Expert panel of four testers. n.d.= not determined.

[0052] The analysis presented in Table 7 indicates that the apple flavor produced by the instant method was as stable as a conventional spray-dried composition at 21°C (12 weeks) or 32°C (12 weeks). However, the impact of the apple flavor produced by the instant method was stronger after storage at 32°C for 12 weeks than that of the conventional spray-dried composition stored at 21°C for 12 weeks.

[0053] The results of prototype mint-flavored gum, as compared to a control, are presented in Table 8.

TABLE 8

Mint Flavored Gum	Prototype Flavor Stability			Control Flavor Stability		
	32°C		21°C	32°C		21°C
	2 weeks	12 weeks	12 weeks	2 weeks	12 weeks	12 weeks
Peppermint	6	4.5	5.5	4.5	3	3.5
Menthol	5.5	4.5	5.5	5.5	3	3.5
Sweet Creamy	5	4	4.5	4.5	3.5	3.5
Sweet	n.d.	6.5	7	n.d.	6	7
Bitter	n.d.	1	1	n.d.	1	1
Astringent	n.d.	1	1	n.d.	1	1
Off-note (plastic)	n.d.	0	0	n.d.	1	3

Scale: 10-point scale (10=highest). Four testers. n.d.= not determined.

[0054] The analysis presented in Table 8 indicates that the mint flavor produced by the instant method was as stable as a conventional spray-dried composition at 21°C (12 weeks) or 32°C (12 weeks). However, the impact of the mint flavor produced by the instant method was stronger after storage at 32°C for 12 weeks than that of the conventional spray-dried composition stored at 21°C for 12 weeks.
Overall, the results of this analysis indicated that the desirable sensory attributes of apple and mint flavors were better maintained in chewing gum using the prototype flavor over 12 weeks at 32°C.

Example 6: Stability of Raspberry Flavor in Powdered Soft Drink Mix

[0055] The stability of raspberry flavor in powdered soft drink mix was evaluated. A raspberry flavor composition was spray-dried in accordance with the instant method, incorporated into a powdered soft drink mix, and the stability of the flavor was evaluated by an expert panel after storage for 8 weeks at 38°C. The results of the prototype soft drink mix containing the instant spray-dried flavor composition, as compared to a control, are presented in Table 9. The control sample was a spray dry flavor processed using conventional drying conditions.

TABLE 9

Sample	Degree of Difference*	Description
Prototype	9	No off-notes present. Flavor attributes similar to refrigerated reference.
Control	7	Lacking fullness, sweetness, loss of impact and juiciness compared to refrigerated reference.

*Scale: 1-3: very large difference, off-notes present; 10: not different from refrigerated reference.

[0056] This analysis indicated that after 8 weeks of accelerated storage, the raspberry prototype maintained flavor quality.

Example 7: Evaluation of Savory Broths

[0057] Spray-dried flavor compositions, prepared in accordance with the instant method, were incorporated into savory broths and attributes of the broths were assessed by a panel of consumers. The attributes of the prototype broths, as compared to a control, are presented in Table 10. The control broths were prepared from spray dry flavors processed using conventional drying conditions.

TABLE 10

Flavor Type	% Preference for Prototype*	Attributes** Prototype vs. Control
Chicken	77 (N=65, p=0.0001)	More white meat flavor, fresher, more balanced, rounder flavor, more overall aroma
Beef	59 (N=63, p=0.17)	More overall aroma, more roasted flavor, bolder flavor, more memorable

*Paired comparison forced choice preference test among category users.
**Significantly different at greater than or equal to 90% confidence interval.

[0058] Consumer data showed statistically significant preference for the prototype flavors. This is further supported by the attributes selected by consumers to describe the flavor quality of the prototypes.

Example 8: Sensory Stability of Neat Powders in High Barrier Packaging

[0059] The stability of various flavor prototypes in high barrier packaging (FRESHTEK) was assessed after storage for 6, 12, or 18 weeks at 40°C. The attributes of the prototype powders are presented in Table 11.

TABLE 11

Prototype	Description*		
	6 weeks	12 weeks	18 weeks
Peach 11-71	Acceptable	Acceptable	Acceptable
Apple 11-58	Acceptable	Acceptable Slight off-notes	Borderline Slight off-notes, noticeably weaker than reference
Orange Valencia 11-299	Acceptable	Acceptable No oxidized notes	Acceptable No oxidized notes
Lime 11-331	Acceptable	Acceptable No oxidized notes, slightly weaker than reference	Borderline No oxidized notes, noticeably weaker than reference
Lemon Brazilian 11-315	Acceptable	Acceptable No oxidized notes	Acceptable No oxidized notes

*Expert panel evaluation, reference sample was kept frozen during storage study.

What is claimed is:

1. A spray-dried flavor composition comprising a spray-dried flavor that contains volatile compounds wherein the volatile compounds are present in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

2. The spray-dried flavor composition of claim 1, wherein the volatile compounds are acetaldehydes, dimethyl sulfides, ethyl acetates, ethyl propionates, methyl butyrates, or ethyl butyrates.

3. The spray-dried flavor composition of claim 1, wherein the volatile compounds have a boiling point of less than 200°C, less than 100°C, or less than 60°C.

4. The spray-dried flavor composition of claim 1, further comprising a carrier material.

5. The spray-dried flavor composition of claim 1, wherein the water activity of the composition is in the range of 0.1 to 0.6 or in the range of 0.2 to 0.4.

5. The spray-dried flavor composition of claim 1, wherein said composition provides a high intensity flavor.

6. The spray dried flavor composition of claim 5, wherein the high intensity flavor is incorporated into gums, confections, oral care products, beverages, snacks, dairy products, soups, sauces, condiments, detergents, fabric softeners and other fabric care products, antiperspirants, deodorants, talc, kitty litter, hair care

and styling products, personal care products, air fresheners, cereals, baked goods or cleaners.

7. The spray dried flavor composition of claim 5, wherein the high intensity flavor is incorporated into a chewing gum or beverage.

8. A spray-dried flavor composition produced by spray drying a flavor that contains volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

9. The spray-dried flavor composition of claim 8, wherein the spray-dried flavor composition is further dried in a fluid bed chamber attached at the spray dryer outlet, wherein the temperature of the air of the fluid-bed unit is at or below the outlet temperature of the spray dryer.

10. The spray-dried flavor composition of claim 8, wherein the volatile compounds are acetaldehydes, dimethyl sulfides, ethyl acetates, ethyl propionates, methyl butyrates, or ethyl butyrates.

11. The spray-dried flavor composition of claim 8, wherein the volatile compounds have a boiling point of less than 200°C, less than 100°C , or less than 60°C.

12. The spray-dried flavor composition of claim 8, wherein the flavor further comprises a carrier material.

13. The spray-dried flavor composition of claim 8 or 12, wherein the flavor further comprises a solvent.

14. The spray-dried flavor composition of claim 13, wherein the solvent is a volatile solvent.

15. The spray-dried flavor composition of claim 13, wherein the flavor and carrier material comprise 40% and 70% as dry solid material of the total composition.

16. The spray-dried flavor composition of claim 13, wherein said flavor is prepared as an emulsion and the volatile compounds are present in the emulsion in an amount that is at least 80% of the volatile compounds originally contained in the flavor.

17. The spray-dried flavor composition of claim 8, wherein air of the spray dryer is partially or wholly nitrogen or carbon dioxide.

18. The spray-dried flavor composition of claim 8, wherein the air inlet temperature is in the range of 40°C to 99°C.

19. The spray-dried flavor composition of claim 8, wherein the water activity of the composition is in the range of 0.1 to 0.6.

20. The spray-dried flavor composition of claim 8, wherein said composition provides a high intensity flavor.

21. The spray-dried flavor composition of claim 20, wherein the high intensity flavor is incorporated into

gums, confections, oral care products, beverages, snacks, dairy products, soups, sauces, condiments, detergents, fabric softeners and other fabric care products, antiperspirants, deodorants, talc, kitty litter, hair care and styling products, personal care products, air fresheners, cereals, baked goods or cleaners.

22. The spray-dried flavor composition of claim 20, wherein the high intensity flavor is incorporated into a chewing gum or beverage.

23. A stable spray-dried flavor composition produced by spray drying a flavor that that contains volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

24. The stable spray-dried flavor composition of claim 23, wherein the stable spray-dried flavor composition is further dried in a fluid bed chamber attached at the spray dryer outlet, wherein the temperature of the air of the fluid-bed unit is at or below the outlet temperature of the spray dryer.

25. The stable spray-dried flavor composition of claim 23, wherein the volatile compounds are acetaldehydes, dimethyl sulfides, ethyl acetates, ethyl propionates, methyl butyrates, or ethyl butyrates.

26. The stable spray-dried flavor composition of claim 23, wherein the volatile compounds have a boiling point of less than 200°C, less than 100°C , or less than 60°C.

27. The stable spray-dried flavor composition of claim 23, wherein the flavor further comprises a carrier material.

28. The stable spray-dried flavor composition of claim 23 or 27, wherein the flavor further comprises a solvent.

29. The stable spray-dried flavor composition of claim 28, wherein the solvent is a volatile solvent.

30. The stable spray-dried flavor composition of claim 28, wherein the flavor and carrier material comprise 40% and 70% as dry solid material of the total composition.

31. The stable spray-dried flavor composition of claim 28, wherein said flavor is prepared as an emulsion and the volatile compounds are present in the emulsion in an amount that is at least 80% of the volatile compounds originally contained in the flavor.

32. The stable spray-dried flavor composition of claim 23, wherein air of the spray dryer is partially or wholly nitrogen or carbon dioxide.

33. The stable spray-dried flavor composition of claim 23, wherein the air inlet temperature is in the range of 40°C to 99°C.

34. The stable spray-dried flavor composition of claim 23, wherein the water activity of the composition is in the range of 0.1 to 0.6.

35. The stable spray-dried flavor composition of claim 23, wherein said composition provides a high intensity flavor.

36. The stable spray-dried flavor composition of claim 35, wherein the high intensity flavor is incorporated into gums, confections, oral care products, beverages, snacks, dairy products, soups, sauces, condiments, detergents, fabric softeners and other fabric care products, antiperspirants, deodorants, talc, kitty litter, hair care and styling products, personal care products, air fresheners, cereals, baked goods or cleaners.

37. The stable spray-dried flavor composition of claim 35, wherein the high intensity flavor is incorporated into a chewing gum or beverage.

38. A method for producing a spray-dried composition capable of retaining volatile compounds comprising spray drying a flavor containing volatile compounds in a spray dryer having an inlet temperature of less than 100°C and an air inlet dew point -10°C to 5°C to obtain a spray-dried flavor composition, wherein the volatile compounds are present in the spray-dried flavor composition in an amount that is at least 20% of the volatile compounds originally contained in the flavor.

39. The method of claim 38, further comprising drying the spray-dried flavor composition in a fluid-bed chamber

attached at the spray dryer outlet, wherein the temperature of the air of the fluid-bed unit is at or below the outlet temperature of the spray dryer.

40. The method of claim 38, wherein the volatile compounds are acetaldehydes, dimethyl sulfides, ethyl acetates, ethyl propionates, methyl butyrates, or ethyl butyrates.

41. The method of claim 38, wherein the volatile compounds have a boiling point of less than 200°C, less than 100°C, or less than 60°C.

42. The method of claim 38, wherein the flavor further comprises a carrier material.

43. The method of claim 38 or 42, wherein the flavor further comprises a solvent.

44. The method of claim 43, wherein the solvent is a volatile solvent.

45. The method of claim 43, wherein the flavor and optional carrier material comprise 40% and 70% as dry solid material of the total composition.

46. The method of claim 43, further comprising preparing the flavor as an emulsion, wherein the volatile compounds are present in the emulsion in an amount that is at least 80% of the volatile compounds originally contained in the flavor.

47. The method of claim 38, wherein the air inlet temperature is in the range of 40°C to 99°C.

48. The method of claim 38, wherein the water activity of the spray-dried flavor composition is in the range of 0.1 to 0.6.

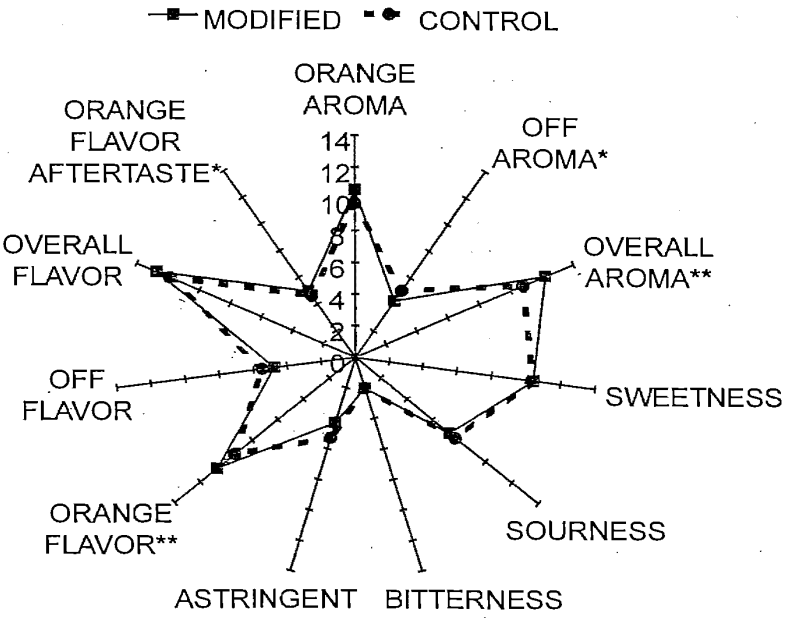
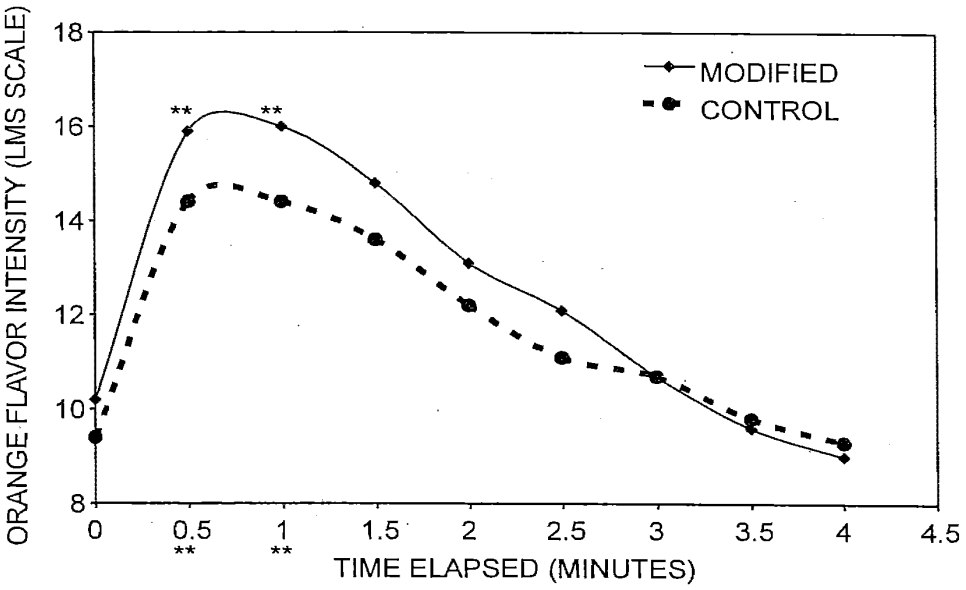


FIG. 1



** SIGNIFICANTLY DIFFERENT AT P = 0.05 AT THESE ELAPSED TIMES

FIG. 2

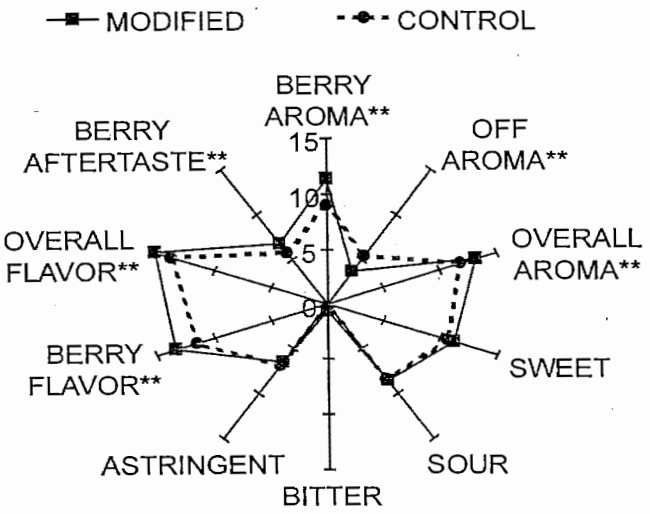
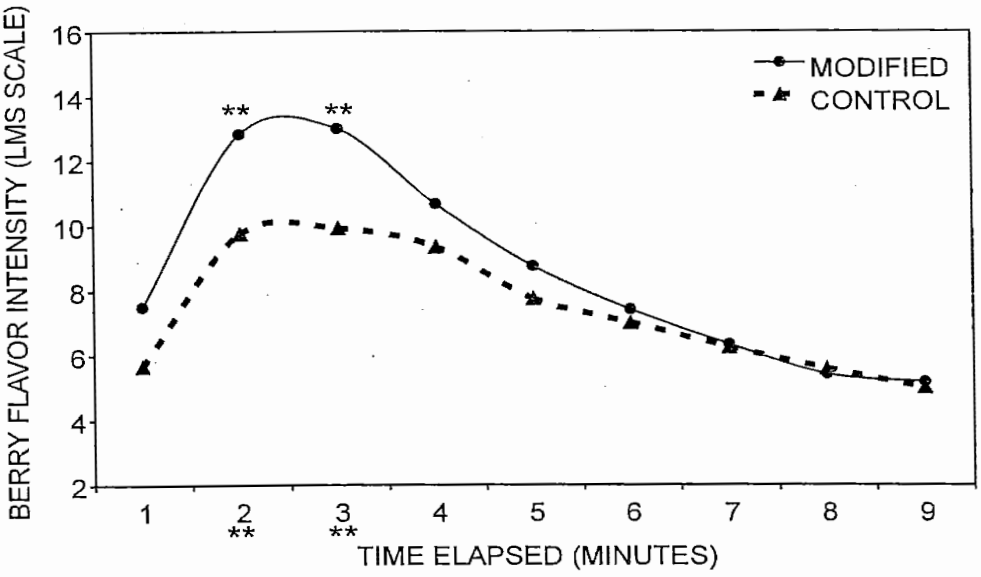


FIG. 3



** SIGNIFICANTLY DIFFERENT AT P=0.05 AT THESE ELAPSED TIMES

FIG. 4

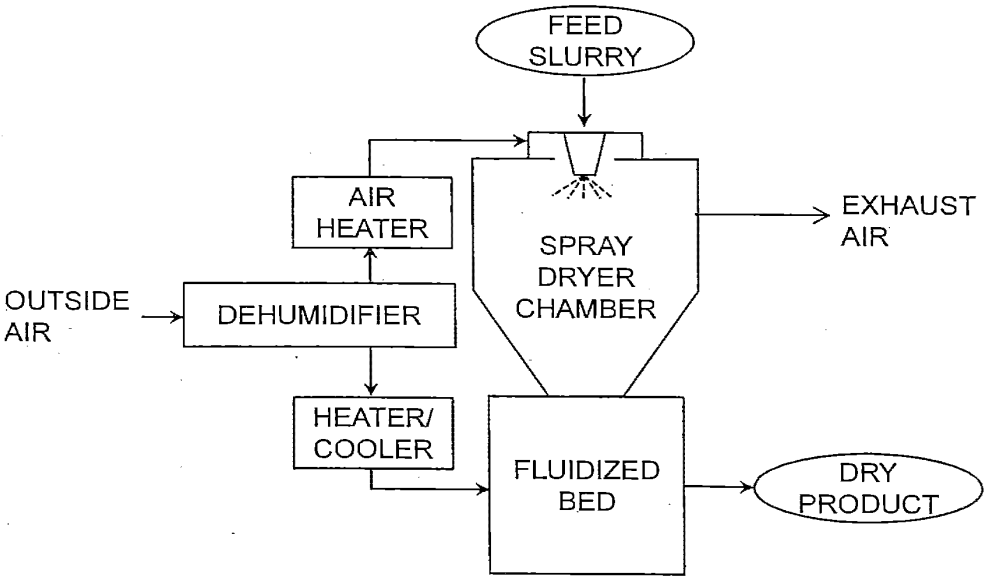

FEED SLURRY
AIR HEATER
SPRAY DRYER CHAMBER
EXHAUST AIR
OUTSIDE AIR
DEHUMIDIFIER
HEATER/ COOLER
FLUIDIZED BED
DRY PRODUCT

FIG. 5

Electronic Acknowledgement Receipt

EFS ID:	21949273
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	02-APR-2015
Filing Date:	27-JAN-2015
Time Stamp:	16:18:34
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101-CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Examiner:**	**Not Yet Assigned**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**	**Customer No.:**	**23448**

CERTIFICATE OF EFS FILING

I hereby certify that this document is being filed via EFS in the United States Patent and Trademark Office on **March 22, 2015**.
/steven j. hultquist/

SUBMISSION OF UPDATED APPLICATION DATA SHEET IN U.S. PATENT APPLICATION NO. 14/606,771

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

Enclosed and submitted herewith is an Updated Application Data Sheet updating the address information for inventor **David Salem** as follows:

~~**2761 Belgarde Blvd. #301**~~

3930 Ridgemoor Drive

Rapid City, SD 57702

and updating the status of the Applicant to **Assignee** from the previously filed status of **Person to whom the inventor is obligated to assign**. The Assignee information has also been set out in the Assignee Information section of the enclosed Updated Application Data Sheet.

It is respectfully requested that the updated information set out in the enclosed Updated Application Data Sheet be entered into the USPTO records for the subject application.

Respectfully submitted,

/steven j. hultquist/
Steven J. Hultquist
Reg. No. 28,021
Attorney for Applicant

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Attorney File No.: 4585-101-CIP

Enclosures:
Updated Application Data Sheet [7 pages]

The USPTO is hereby authorized to charge any deficiency or credit any overpayment of fees properly payable for this document to Deposit Account No. 08-3284

PTO/AIA/14 (12-13)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Charles	P.	Beetz	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Erlanger	State/Province	KY	Country of Residence	US

Mailing Address of Inventor:

Address 1	878 Borderlands Dr.		
Address 2			
City	Erlanger	State/Province	KY
Postal Code	41018	Country	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Robert		Corbett	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Westfield	State/Province	NJ	Country of Residence	US

Mailing Address of Inventor:

Address 1	779 Hyslip Avenue		
Address 2			
City	Westfield	State/Province	NJ
Postal Code	07090	Country	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	David		Salem	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

City	Rapid City	State/Province	SD	Country of Residence	US

Mailing Address of Inventor:

Address 1	~~2761 Belgarde Blvd. #301~~ 3930 Ridgemoor Drive		
Address 2			
City	Rapid City	**State/Province**	SD
Postal Code	57702	**Country**	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	23448		
Email Address	hip@hultquistip.com	Add Email	Remove Email

Application Information:

Title of the Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING		
Attorney Docket Number	4585-101-CIP	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	17	**Suggested Figure for Publication (if any)**	

Filing By Reference :

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☒ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	(●) Customer Number	( ) US Patent Practitioner	( ) Limited Recognition (37 CFR 11.9)
Customer Number	23448		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Patented				Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
	Continuation in part of	13/245369	2011-09-26	8939388	2015-01-27

Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
13/245369	Claims benefit of provisional	61/386762	2010-09-27

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☐ Authorization to Permit Access to the Instant Application by the Participating Offices

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date o f filing this Authorization.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

(•) Assignee	( ) Legal Representative under 35 U.S.C. 117	( ) Joint Inventor
( ) Person to whom the inventor is obligated to assign.	( ) Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :	

If the Applicant is an Organization check here. ☒

Organization Name	ZoomEssence, Inc.

Mailing Address Information For Applicant:

Address 1	550 Hartle Street, Unit B		
Address 2			
City	Sayreville	**State/Province**	NJ
Country	US	Postal Code	08872
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not subsitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☒

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Organization Name	ZoomEssence, Inc.		
Mailing Address Information For Assignee including Non-Applicant Assignee:			
Address 1	550 Hartle Street, Unit B		
Address 2			
City	Sayreville	**State/Province**	NJ
Country i	US	Postal Code	08872
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Signature	/steven j. hultquist/			Date (YYYY-MM-DD)	2015-03-19
First Name	Steven J.	Last Name	Hultquist	Registration Number	28021

Additional Signature may be generated within this form by selecting the Add button.

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent C o o p eration Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	21841540
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. Beetz
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	22-MAR-2015
Filing Date:	27-JAN-2015
Time Stamp:	15:32:52
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Miscellaneous Incoming Letter	101CIP_SubmissionUpdatedADS.pdf	21252 52bdab3a910b30f0017bef3d0b8c398186bf7873	no	2

Warnings:	
Information:	

2	Application Data Sheet	101CIP_UpdatedApplicationDataSheet.pdf	2257820 7180fff0afd5798d01a71a163133d4653395675c	no	7

Warnings:	
Information:	
This is not an USPTO supplied ADS fillable form	
Total Files Size (in bytes):	2279072

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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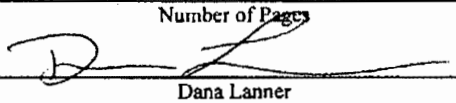
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:		**Docket No.:**	**4585-101-CIP**
Applicant:	**ZOOMESSENCE, INC.**	**Conf. No.:**	**9733**
Application No.:	**14/606,771**	**Art Unit:**	**3752**
Date Filed:	**January 27, 2015**	**Customer No.:**	**23448**
Title:	**METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING**		

FACSIMILE TRANSMISSION CERTIFICATE
Fax No. (571) 273-8300

I hereby certify that this document is being filed in the United States Patent and Trademark Office, via facsimile transmission addressed to Mail Stop Missing Parts, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, and transmitted on the date specified below, to United States Patent and Trademark Office facsimile transmission number (571) 273-8300.

5
Number of Pages



Dana Lanner

March 19, 2015
Date

SUBMISSION OF DECLARATION DOCUMENT IN U.S. PATENT APPLICATION NO. 14/606,771

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

MAR 19 2015

Sir:

Enclosed and submitted herewith is an executed Declaration document for the above-identified U.S. patent application. An executed Declaration was filed at the time of filing the subject application, thus, no fees are due for the filing of this document.

Respectfully submitted,

Steven J. Hultquist
Reg. No. 28,021
Attorney for Applicant

HULTQUIST IP
P.O. Box 14329
Research Triangle Park, NC 27709
Phone: (919) 419-9350
Fax: (919) 419-9354
Attorney File No.: 4585-101-CIP

Enclosures:
Executed Declaration Document [3 pgs.]

The USPTO is hereby authorized to charge any deficiency or credit any overpayment of fees properly payable for this document to Deposit Account No. 08-3284

PAGE 2/5 * RCVD AT 3/19/2015 12:41:58 PM [Eastern Daylight Time] * SVR:W-PTOFAX-001/5 * DNIS:2738300 * CSID:19194199354 * DURATION (mm-ss):02-04

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

As the below named inventor, I hereby declare that:

This declaration is directed to:

- [ ] The attached application, or
- [X] United States application or PCT international application number 14/606,771 filed on January 27, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

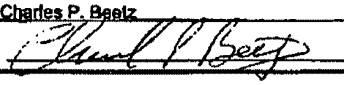
I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Charles P. Beetz Date (Optional): _____

Signature: 

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comment on the amount of time you required to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

As the below named inventor, I hereby declare that:

This declaration is directed to:

- [ ] The attached application, or
- [x] United States application or PCT international application number 14/606,771 filed on January 27, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published applications or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Robert Corbett Date (Optional): _____

Signature: Robert Corbett

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comment on the amount of time you required to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 14/606,771 filed on January 27, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published applications or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: David Salem Date (Optional): _____

Signature: _____

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comment on the amount of time you required to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 14/606,771

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	70		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	300		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*	x 210 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	730		TOTAL	

APPLICATION AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
14/606,771	01/27/2015	1761	730	4585-101 CIP	20	3

CONFIRMATION NO. 9733

23448
Hultquist IP
P.O. Box 14329
RESEARCH TRIANGLE PARK, NC 27709

FILING RECEIPT

OC000000073400421

Date Mailed: 02/17/2015

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Charles P. Beetz, Erlanger, KY;
Robert Corbett, Westfield, NJ;
David Salem, Rapid City, SD;

Applicant(s)

ZoomEssence, Inc., Sayreville, NJ

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CIP of 13/245,369 09/26/2011 PAT 8939388
which claims benefit of 61/386,762 09/27/2010

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

If Required, Foreign Filing License Granted: 02/12/2015

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/606,771**

Projected Publication Date: Request for Non-Publication Acknowledged

Non-Publication Request: Yes

Early Publication Request: No
**** SMALL ENTITY ****

Title

METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

Preliminary Class

510

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

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The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

DocCode – SCORE

SCORE Placeholder Sheet for IFW Content

Application Number: 14606771 Document Date: 01/27/2015

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

Since this was an electronic submission, there is no physical artifact folder, no artifact folder is recorded in PALM, and no paper documents or physical media exist. The TIFF images in the IFW record were created from the original documents that are stored in SCORE.

- Drawing

At the time of document entry (noted above):

- USPTO employees may access SCORE content via eDAN using the Supplemental Content tab, or via the SCORE web page.
- External customers may access SCORE content via PAIR using the Supplemental Content tab.

Form Revision Date: August 26, 2013

PTO/AIA/15 (03-13)
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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	4585-101-CIP
First Named Inventor	Beetz, Charles P.
Title	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
Express Mail Label No.	

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. [ ] **Fee Transmittal Form** (PTO/SB/17 or equivalent)
2. [X] **Applicant asserts small entity status.** See 37 CFR 1.27.
3. [ ] **Applicant certifies micro entity status.** See 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent.
4. [X] **Specification** [*Total Pages* 28] Both the claims and abstract must start on a new page *(See MPEP § 608.01(a)) for information on the preferred arrangement)*
5. [X] **Drawing(s)** *(35 U.S.C. 113)* [*Total Sheets* 17]
6. **Inventor's Oath or Declaration** [*Total Sheets* 4] *(including substitute statements under 37 CFR 1.64 and assignments serving as an oath or declaration under 37 CFR 1.63(e))*
   a. [ ] Newly executed (original or copy)
   b. [X] A copy from a prior application (37 CFR 1.63 (d))
7. [X] **Application Data Sheet** **See Note Below.* See 37 CFR 1.76 (PTO/AIA/14 or equivalent)
8. [ ] **CD-ROM or CD-R** in duplicate, large table or Computer Program *(Appendix)*
   [ ] Landscape Table on CD
9. **Nucleotide and/or Amino Acid Sequence Submission.** (*if applicable, items a. – c. are required*)
   a. [ ] Computer Readable Form (CRF)
   b. [ ] Specification Sequence Listing on:
      i. [ ] CD-ROM or CD-R (2 copies); or
      ii. [ ] Paper
   c. [ ] Statements verifying identity of above copies

ADDRESS TO:

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

ACCOMPANYING APPLICATION PAPERS

10. [ ] **Assignment Papers** (cover sheet & document(s))
    Name of Assignee_____
11. [ ] **37 CFR 3.73(c) Statement** [ ] **Power of Attorney** (*when there is an assignee*)
12. [ ] **English Translation Document** *(if applicable)*
13. [ ] **Information Disclosure Statement** (PTO/SB/08 or PTO-1449)
    [ ] Copies of citations attached
14. [ ] **Preliminary Amendment**
15. [ ] **Return Receipt Postcard** *(MPEP § 503) (Should be specifically itemized)*
16. [ ] **Certified Copy of Priority Document(s)** *(if foreign priority is claimed)*
17. [X] **Nonpublication Request** under 35 U.S.C. 122 (b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent.
18. [ ] **Other:**

_____

***Note:** (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 **must** be included in an Application Data Sheet (ADS).
(2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

19. CORRESPONDENCE ADDRESS

[X] The address associated with Customer Number: 23448 *OR* [ ] Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone		Email	

Signature	*/steven j. hultquist/*	Date	January 27, 2015
Name (Print/type)	*Steven J. Hultquist*	Registration No. (Attorney/Agent)	28021

This collection of information is required by 37 CFR 1.53(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.** *If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

PTO/AIA/14 (12-13)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Charles	P.	Beetz	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Erlanger	State/Province	KY	Country of Residence	US

Mailing Address of Inventor:

Address 1	878 Borderlands Dr.
Address 2	

City	Erlanger	State/Province	KY
Postal Code	41018	Country	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Robert		Corbett	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Westfield	State/Province	NJ	Country of Residence	US

Mailing Address of Inventor:

Address 1	779 Hyslip Avenue
Address 2	

City	Westfield	State/Province	NJ
Postal Code	07090	Country	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	David		Salem	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

PTO/AIA/14 (12-13)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

City	Rapid City	State/Province	SD	Country of Residence	US

Mailing Address of Inventor:

Address 1	2761 Belgarde Blvd. #301		
Address 2			
City	Rapid City	**State/Province**	SD
Postal Code	57702	**Country**	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	23448		
Email Address	hip@hultquistip.com	Add Email	Remove Email

Application Information:

Title of the Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING		
Attorney Docket Number	4585-101-CIP	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	17	**Suggested Figure for Publication (if any)**	

Filing By Reference :

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☒ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	(●) Customer Number	( ) US Patent Practitioner	( ) Limited Recognition (37 CFR 11.9)
Customer Number	23448		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Patented			Remove	
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
	Continuation in part of	13/245369	2011-09-26	8939388	2015-01-27

Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
13/245369	Claims benefit of provisional	61/386762	2010-09-27

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

			Remove
Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☐ Authorization to Permit Access to the Instant Application by the Participating Offices

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date o f filing this Authorization.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

○ Assignee	○ Legal Representative under 35 U.S.C. 117	○ Joint Inventor
◉ Person to whom the inventor is obligated to assign.	○ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. ☒

Organization Name	ZoomEssence, Inc.		
Mailing Address Information For Applicant:			
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City	Sayreville	**State/Province**	NJ
Country	US	Postal Code	08872
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not subsitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4585-101-CIP
	Application Number	
Title of Invention	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING	

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country [i]		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Signature	/steven j. hultquist/			Date (YYYY-MM-DD)	2015-01-27
First Name	Steven J.	Last Name	Hultquist	Registration Number	28021

Additional Signature may be generated within this form by selecting the Add button.

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent C o o p eration Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

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Declaration and Power of Attorney

As a below named inventor, I hereby declare:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the following invention:

Title: Methods And Apparatus For Low heat Spray Drying

__x__The specification of which is attached hereto.

_____The specification of which was filed on _____

as Application Serial No. _____

and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I hereby claim foreign priority benefits under 35 U.S.C. §§ 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America.

Prior Foreign Application(s):

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint all practitioners of Gibson & Dernier LLP associated with **Customer Number 27538** jointly and severally as my attorneys and/ or agents with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Direct correspondence to: Matthew B. Dernier, Esq. at the address associated with **Customer Number 27538**.

Full name of **FIRST NAMED INVENTOR**:	Charles P. Beetz
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Inventor's Signature:	Robert Corbett
Date:	9/15/11
Residence:	Westfield, NJ
Citizenship:	U.S.
Post Office Address:	779 Hyslip Avenue Westfield, NJ 07090
Full name of **THIRD NAMED INVENTOR**:	David Salem
Inventor's Signature:	
Date:	
Residence:	Rapid City, SD
Citizenship:	U.S.
Post Office Address:	2761 Belgarde Blvd. #301 Rapid City, SD 57702

Declaration and Power of Attorney

As a below named inventor, I hereby declare:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the following invention:

Title: Methods And Apparatus For Low heat Spray Drying

__x__The specification of which is attached hereto.

_____The specification of which was filed on _____

as Application Serial No. _____

and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I hereby claim foreign priority benefits under 35 U.S.C. §§ 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America.

Prior Foreign Application(s):

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint all practitioners of Gibson & Dernier LLP associated with **Customer Number 27538** jointly and severally as my attorneys and/ or agents with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Direct correspondence to: Matthew B. Dernier, Esq. at the address associated with **Customer Number 27538**.

Full name of **FIRST NAMED INVENTOR**: Charles P. Beetz

Inventor's Signature: _____

Date: _____

Residence: Erlanger, KY

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Erlanger, KY 41018

Full name of **SECOND NAMED INVENTOR**: Robert Corbett

Inventor's Signature: _____

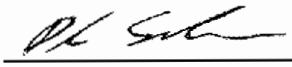
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Full name of **THIRD NAMED INVENTOR**: David Salem

Inventor's Signature: 

Date: 9/26/2011

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Citizenship: U.S.

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NONPUBLICATION REQUEST UNDER 35 U.S.C. 122(b)(2)(B)(i)

First Named Inventor	Beetz, et al.
Title	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
Attorney Docket Number	4585-101-CIP

I hereby certify that the invention disclosed in the attached application **has not and will not be** the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

I hereby request that the attached application not be published under 35 U.S.C. 122(b).

/steven j. hultquist/ — Signature

January 27, 2015 — Date

Steven J. Hultquist — Typed or printed name

28021 — Registration Number, if applicable

(919) 419-9350 — Telephone Number

This request must be signed in compliance with 37 CFR 1.33(b) and submitted with the application **upon filing.**

Applicant may rescind this nonpublication request at any time. If applicant rescinds a request that an application not be published under 35 U.S.C. 122(b), the application will be scheduled for publication at eighteen months from the earliest claimed filing date for which a benefit is claimed.

If applicant subsequently files an application directed to the invention disclosed in the attached application in another country, or under a multilateral international agreement, that requires publication of applications eighteen months after filing, the applicant **must** notify the United States Patent and Trademark Office of such filing within forty-five (45) days after the date of the filing of such foreign or international application. **Failure to do so will result in abandonment of this application (35 U.S.C. 122(b)(2)(B)(iii)).**

This collection of information is required by 37 CFR 1.213(a). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 6 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**.

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.

UNITED STATES PATENT APPLICATION

OF

CHARLES P. BEETZ

ROBERT CORBETT

AND

DAVID SALEM

FOR

METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

CERTIFICATE OF EFS FILING

I hereby certify that this patent application is being filed via EFS in the United States Patent and Trademark Office on January 27, 2015.

/steven j. hultquist/

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METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a continuation-in-part under 35 USC 120 of United States Patent Application No. 13/245,369 filed September 26, 2011 in the names of Charles P. Beetz, Robert Corbett, and David Salem for "METHODS AND APPRATUS FOR LOW HEAT SPRAY DRYING," and issued January 27, 2015 as U.S. Patent 8,939,388, which in turn claims the benefit under 35 USC 119 of U.S. Provisional Patent Application No. 61/386,762, filed September 27, 2010 in the names of Charles P. Beetz, Robert Corbett, and David Salem for "METHODS AND APPRATUS FOR LOW HEAT SPRAY DRYING." The disclosures of United States Patent Application No. 13/245,369 and U.S. Provisional Patent Application No. 61/386,762 are hereby incorporated herein by reference in their respective entireties, for all purposes.

FIELD

[0002] The present disclosure relates to methods and apparatus for spray drying a liquid product into a dried powder without applying heat, or applying substantially low amounts of heat.

DESCRIPTION OF THE RELATED ART

[0003] Spray drying is a method of producing a dry powder from a liquid or slurry by rapidly drying with a hot gas (usually air). Spray drying technology has existed since the late 1800's and has continually evolved over the past century.

[0004] The spray drying process begins with a liquid solvent, commonly water, containing dissolved or suspended components such as an emulsion. The suspension includes a substance to be encapsulated (the load) and an amphipathic carrier (usually some sort of modified starch), which are homogenized as a suspension in the liquid solvent. The load is typically some constituent component(s) of a food, fragrance, medicament, etc., and the homogenized suspension is often referred to as a slurry.

[0005] Spray dryers use some type of atomizer, such as a spray nozzle, to disperse the slurry into a controlled spray having some relatively controlled droplet size. Depending on the process requirements, droplet sizes may range from about 10 to 500 microns in diameter. The most common applications require droplet sizes in the 50 to 200 micron range.

[0006] In conjunction with atomization, the slurry is fed into a drying chamber, usually a tower into which heated air is also introduced. The temperature of the air as it enters the drying chamber is well over the boiling point of water, usually in the range of 180-200 °C. The heated air supplies energy for evaporation of volatile components of the liquid (the water) from the droplets. As the water evaporates, the carrier forms a hardened shell around the load, producing a dried powder.

[0007] Reference is made to FIG. 1, which illustrates a conventional spray drying system 50 and associated process. The process begins with making a slurry of ingredients. The ingredients include a liquid solvent, such as water 1, a carrier 2, and active ingredient(s) 3. In the typical process, the water 1 and carrier 2 are added into the solution tank 4 while stirring. The active ingredient 3 is then added to the tank 4 and stirred into the slurry. The active ingredient is either emulsified in the carrier fluid system or dissolved into it. In order for conventional spray drying processes to be commercially viable, typical slurry viscosities must be in the range of about 10-300 mPa-s.

[0008] The slurry formed in the solution tank 4 is delivered to an atomizer 6 using a feed pump 5 or other means of conveyance. The slurry enters the atomizer 6 and leaves the atomizer as a spray of liquid droplets 8, and the droplets 8 are introduced into a drying chamber 7. Concurrently, a feed of air is heated by a process heater 11 and supplied into the drying chamber 7 by a blower 10. The water evaporated from the droplets 8 enters the heated air as the atomized liquid droplets 8 dry to form solid particles after exposure to the incoming heated air.

[0009] The dried powder leaves the dryer chamber 7 along with the water vapor laden air, and is carried to a cyclone separator 12, which removes the dried particles from the circulating air stream and deposits the particles into a collection container 13. The water vapor laden air exits the collection container 13 and enters a baghouse 14, where very fine particles are removed before the water vapor laden air is sent into a condenser 9, via blower 15. The condenser 9 removes the water vapor from the process air, and the collected water may be re-used or discarded.

[0010] One of the prominent attributes of the traditional spray drying process is the high temperature of the inlet gas (typically on the order of 200 °C) leaving the heater 11 and entering the drying chamber 7, as well as the temperature of the outlet gas exiting the drying chamber 7, which is usually in excess of 100 °C. Although the liquid droplets 8 are injected into the high temperature environment within the chamber 7, the droplets 8 do not actually reach the inlet gas temperature. The droplets 8, however, do become heated to a point at which considerable portions of desired constituents of the droplets (i.e., portions of the load) are undesirably

modified, such as evaporated and/or oxidized. The undesirable modification to the load (load loss) leads to a reduction in flavor (in the case of food loads), a reduction in aroma (in the case of fragrances), etc. Essentially, evaporation and heat degradation of the load lowers the performance characteristics of the final powder product, and therefore results in a significant degradation of performance in commercial use and a significant loss of revenue.

[0011] The above disadvantageous characteristics of the conventional spray dry process have resulted in many process modifications and emulsion formulations to compensate for heat induced alterations in the load. This is especially true in the pharmaceutical industry, where excessive heating during spray drying leads to degradation of the active ingredient in a powdered medicament. This also presents a challenge to flavorists in the powdered flavor industry to design flavor formulations that can survive the drying process and deliver acceptable (although significantly flawed) flavor characteristics.

[0012] In view of the above, there are needs in the art for new methods and apparatus for carrying out the spray drying process, which reduce or eliminate the disadvantageous characteristics of the conventional spray dry process.

SUMMARY

[0013] Methods and apparatus for spray drying a liquid product into a dried powder without applying heat provide for: forming a slurry including a liquid solvent, a carrier, and an active ingredient; applying an electrostatic charge to the slurry; atomizing the charged slurry to produce a plurality of electrostatically charged, wet particles; suspending the electrostatically charged, wet particles for a sufficient time to permit repulsive forces induced by the electrostatic charge on at least some wet particles to cause at least some of such particles to divide into wet sub-particles; and continuing the suspending step, without the presence of any heated drying fluids, for a sufficient time to drive off a sufficient amount of the liquid solvent within most of the wet particles to leave a plurality of dried particles (the powder), each dried particle containing the active ingredient encapsulated within the carrier.

[0014] Preferably, a temperature of the non-heated drying fluid is less than about 100°C at introduction into the drying chamber, such as at least one of: less than about 75 °C at introduction into the drying chamber; less than about 45 °C at introduction into the drying chamber; less than about 35 °C at introduction into the drying chamber; less than about 30 °C at introduction into the drying chamber; and at about an ambient temperature of a room within which the drying chamber is located.

[0015] The methods and apparatus may further provide for subjecting the electrostatically charged, wet particles to a non-heated drying fluid within a drying chamber to drive off the liquid solvent. Alternatively or additionally, the methods and apparatus may further provide for dehumidifying the non-heated drying fluid prior to introduction into the drying chamber. Alternatively or additionally, the methods and apparatus may further provide for applying one or more electric fields within the drying chamber to urge at least one of the wet particles and the dry particles to travel in a direction defined from an inlet end of the drying chamber to an outlet end of the drying chamber.

[0016] The methods and apparatus may further provide for controlling one or more of a viscosity of the slurry during formation a ratio of water within the slurry during formation, such that one or more of: (i) the viscosity of the slurry at the atomization step is at least one of: greater than about 300 mPa-s; greater than about 350 mPa-s; greater than about 400 mPa-s; greater than about 500 mPa-s; greater than about 600 mPa-s; greater than about 700 mPa-s; between about 500-16,000 mPa-s; and between about 1000-4000 mPa-s; and (ii) the ratio of water within the slurry at the atomization step is at least one of: between about 20-50 weight percentage; between about 20-45 weight percentage; between about 20-45 weight percentage; between about 20-40 weight percentage; about 30 weight percentage.

[0017] The apparatus may include a drying chamber, including an inlet end, an outlet end, and an internal volume within which the liquid product is dried, where the drying chamber is formed from a non-electrically conductive material.

[0018] Additionally or alternatively, a first electrode may be located at or near the inlet end of the drying chamber; and a second electrode may be located at or near the outlet end of the drying chamber, where application of a source of voltage potential between the first and second electrodes induces an electric field within the drying chamber sufficient to urge particles of the liquid product, produced by way of atomization, from the inlet end toward the outlet end of the drying chamber. Preferably, the first and second electrodes are disposed external to the drying chamber, yet induce an electric field within the internal volume of the drying chamber by virtue of the formation of the drying chamber from the non-electrically conductive material.

[0019] The apparatus may additionally or alternatively include a nozzle operating to atomize a slurry to produce a plurality of wet particles, where the slurry includes a liquid solvent, a carrier, and an active ingredient. The apparatus may further include at least one electrode operating to contact the slurry and apply an electrostatic charge thereto, such that the nozzle operates to produce a plurality of electrostatically charged wet particles. The at least one

electrode may be disposed within the nozzle such that the slurry contacts the electrode and becomes electrostatically charged while flowing from an inlet end to an outlet end of the nozzle.

[0020] A dried powder produced using one or more aspects of the invention may include: a plurality of dried particles, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein: the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry; and wherein a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

[0021] Alternatively or additionally, the weight percentage of at least one of the one or more principle molecular types in the final active ingredient may be within about 3%, 2% or 1% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

[0022] Additionally or alternatively, a dried powder produced using one or more aspects of the invention may include: a plurality of dried particles, which individually contain an amount of active ingredient encapsulated within a carrier, wherein: the active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and wherein a weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 5% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

[0023] Additionally or alternatively, the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 3%, 2% or 1% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

[0024] Other aspects, features, and advantages of the present invention will be apparent to one skilled in the art from the description herein taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] For the purposes of illustration, there are forms shown in the drawings that are presently preferred, it being understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown.

[0026] FIG. 1 is a system for spray drying a liquid product into a dried powder through the convention application of heated air in accordance with the prior art;

[0027] FIG. 2 is a system for spray drying a liquid product into a dried powder without employing heated air in accordance with one or more aspects of the present invention;

[0028] FIG. 3 is a cross-sectional view of an atomizer that may be employed in the system of FIG. 2 in order to produce a plurality of droplets from a slurry in accordance with one or more aspects of the present invention;

[0029] FIG. 4 is a cross-sectional view of a distal end of an atomizer that may be employed in the atomizer of FIG. 3 in accordance with one or more aspects of the present invention;

[0030] FIG. 5 is a perspective, exploded view of certain components of the distal end of the atomizer of FIG. 4 in accordance with one or more aspects of the present invention;

[0031] FIG. 6 is a schematic, side view of a drying chamber that may be employed in the system of FIG. 2 in accordance with one or more aspects of the present invention;

[0032] FIG. 7 is an image of dried powder non-fibrous particles produced using the system of FIG. 2;

[0033] FIG. 8 is an image of a cross-section through one of the dried powder particles of FIG. 7 showing the encapsulation of the load within the carrier;

[0034] FIG. 9 is an image of dried powder fibers produced using the system of FIG. 2;

[0035] FIG. 10 is an image of a cross-section through one of the dried powder fibers of FIG. 9 showing the encapsulation of the load within the carrier; and

[0036] FIG. 11 is a graph illustrating certain properties of dried powder particles produced using the system of FIG. 2 as compared with the conventional spray drying process.

[0037] FIGS. 12-19 are graphs illustrating retention of properties by spray dried powders of the present disclosure.

DETAILED DESCRIPTION

[0038] With reference to the drawings, wherein like numerals indicate like elements, there is shown in FIG. 2 a system 100 for spray drying a liquid product into a dried powder without employing heated air in accordance with one or more aspects of the present invention. The

system 100 includes some of the same or similar elements as in the system 50 of FIG. 1, which elements have the same reference designators.

[0039] By way of a high level description, the system 100 includes a drying chamber 107 into which a slurry is fed by way of a feed pump 5 (or equivalent conveying mechanism). The slurry enters an atomizer 106 and leaves the atomizer as a spray of liquid droplets 108, which are introduced into the drying chamber 7. Concurrently, a feed of non-heated fluid (such as air or another suitable gas) is supplied into the drying chamber 107 by a blower 10. The supplied air may be subjected to dehumidification (via dehumidifier 110) prior to introduction into the drying chamber 107. The atomized liquid droplets 108 dry to form solid particles after exposure to the incoming air. Water evaporates from the droplets 108 and enters the air within the drying chamber 107. Dried powder leaves the drying chamber 107 along with the water vapor laden air, and is carried to a cyclone separator 12, which removes the dried particles from the circulating air stream and deposits the particles into a collection container 13. The water vapor laden air exits the collection container 13 and enters a baghouse 14, where very fine particles are removed before the water vapor laden air is sent into a condenser 9, via blower 15. The condenser 9 removes the water vapor from the process air, and the collected water may be re-used or discarded.

[0040] There are a number of very significant differences between the systems of FIGS. 1 and 2. Among these differences is the fact that the system 100 and related spray drying process does not use a heated fluid (e.g., air) to dry the atomized droplets within the drying chamber. The use of non-heated air is directly counter to the conventional and accepted wisdom in the spray drying art. Indeed, there is no known prior art spray drying process or system that does not use significantly heated air (on the order of 200 °C) in the drying process, despite the fact that the load loss associated with the heating process is well understood by skilled artisans. The reason that conventional spray drying processes call for heated air, however, is that artisans have failed to develop an alternative to using heated air that results in suitable (albeit degraded) dried powder product.

[0041] Among the reasons that non-heated air may be used in the spray drying system 100 and process is that the slurry is not conventional. In general, the slurry includes a liquid solvent, a carrier, and an active ingredient. The liquid solvent is usually water, however, other suitable solvents may be employed if needed or desired. The carrier is usually a modified starch. The active ingredient may be any desirable single constituent component or a combination of constituent components, at least one of which is among one or more principle molecular types

from which at least one of a desirable food, flavor, fragrance, medicament, pigment, probiotic, bacteria, etc. is obtained.

[0042] Formation of the slurry is controlled such that regulation of at least one of the viscosity, the amount of liquid solvent (e.g., water), or other suitable metric relating to the water content of the slurry, is obtained. For example, the formation of the slurry may include controlling a viscosity of the slurry such that the viscosity at the atomization step is at least one of: greater than about 300 mPa-s; greater than about 350 mPa-s; greater than about 400 mPa-s; greater than about 500 mPa-s; greater than about 600 mPa-s; greater than about 700 mPa-s; between about 500-16,000 mPa-s; and between about 1000-4000 mPa-s. Additionally or alternatively, the formation of the slurry may include controlling a ratio of water within the slurry such that the ratio of water within the slurry at the atomization step is at least one of: between about 20-50 weight percentage; between about 20-45 weight percentage; between about 20-45 weight percentage; between about 20-40 weight percentage; and about 30 weight percentage. In order to provide some information as to the significant differences between a slurry according to one or more embodiments of the invention and conventional slurries, it is noted that conventional slurries have viscosities between about 10-200 mPa-s and contain an amount of water between about 50-70% by weight.

[0043] Another reason that non-heated air may be used in the spray drying system 100 (and process) relates to an unconventional electrostatic charging process that is conducted before, during or after atomization. In particular, an electrostatic charge is applied to the slurry or to the atomized droplets 108, preferably the former. In this regard, the system 100 includes a high voltage supply 104 (such as about 45 kV DC) that is coupled to one or more electrodes (not shown in FIG. 2). The polarity of the high voltage supply 104 may be in either the positive or negative configuration. The slurry (or atomized droplets 108) is brought into contact with the electrode to impart an electrical charge thereto. In a preferred embodiment, the slurry is brought into contact with the electrode(s) in order to produce a charged slurry. Concurrently or thereafter, the charged slurry is atomized to produce a plurality of electrostatically charged, wet particles (droplets) 108.

[0044] The respective charge on the wet droplets 108 produces a force that tends to cause adjacent droplets to repel one another. Additionally, the force on a given droplet 108 opposes the surface tension of such given droplet 108. When the charge on the given droplet 108 exceeds a threshold level, the Rayleigh limit, the droplet 108 becomes unstable and smaller satellite droplets 108 are ejected from the given (parent) droplet 108. One or more of the satellite droplets 108, in

turn, might also become unstable and produce additional satellite droplets 108, since the surface charge density does not diminish in the satellite droplets 108 as evaporation takes place.

[0045] The electrostatically charged, wet particles/droplets 108 are suspended for a sufficient time within the drying chamber 107 to permit the aforementioned repulsive forces induced by the electrostatic charge on at least some wet particles/droplets 108 to cause at least some of such particles to divide into wet sub-particles/droplets 108. The suspension of the droplets 108 continues, without the presence of any heated drying fluids, for a sufficient time to drive off a sufficient amount of the liquid solvent within most of the wet particles/droplets 108 to leave a plurality of dried particles (the powder), each dried particle containing the active ingredient encapsulated within the carrier. Notably, the production of sub-particles/droplets 108 from a given volume of atomized slurry (i.e., from a given droplet 108) results in faster drying of such volume due to a greatly increased aggregate surface area of the sub-particles/droplets 108 and concomitant reduction of particle volume of each sub-particle/droplet 108 following each fission event.

[0046] The production of sub-particles/droplets 108 may be referred to as coulombic fission. The time scale for such coulombic fission events is on the order of a few microseconds to milliseconds. The fission of about ten (10) sub-particles/droplets 108 from a given particle/droplet 108 reduces a diameter of the given particle/droplet 108 by about 30%. The amount of time that it takes to achieve such reduction in diameter (on the order of a few microseconds to milliseconds) is an order of magnitude faster than diffusive evaporation in the presence of heated air, which occurs with a characteristic time t in accordance with the following formula:

$$t = do^2/k$$

where do is the diameter of the particle and k is the evaporative diffusion coefficient. For particles in the 20 to 200 mm diameter range, the time to any significant diameter reduction by evaporation is on the order of tenths to several seconds, which is far longer (one to two orders of magnitude) than diameter reduction by coulombic fission.

[0047] The individual or combined characteristics of relative low water content in the slurry and electrostatic charge on the droplets 108 permits vastly a different temperature condition within the drying chamber 107 as compared with prior art systems and processes. For example, a temperature of the non-heated drying fluid (air) introduced into the drying chamber 107 may be at least one of: less than about 100 °C; less than about 75 °C; less than about 45 °C; less than about 35 °C; less than about 30 °C; and at about an ambient temperature of a room within which the

drying chamber 107 is located. The above temperature ranges assume a lower limit above freezing.

[0048] It has been demonstrated that an inlet air temperature of about 40°C may result in an outlet air temperature of about 32°C from the drying chamber 107.

[0049] While elevated temperatures as compared to the convention spray drying process of the prior art may not be necessary, it may be desirable to ensure that the drying fluid (air) introduced into the drying chamber 107 is of relatively low water content. Thus, the system 100 may include the process dehumidifier 110 in order to remove some amount of water from the air prior to introduction into the drying chamber 107. After dehumidification, the non-heated air as input into the drying chamber 107 may be at a relative humidity of about 7%.

[0050] The atomizer 106 may be implemented by way of any of the known methods, apparatus, and/or techniques. For example, the atomizer 106 may be implemented using at least one of: a nozzle technique, a centrifugal technique, a pneumatic technique, and an ultrasonic technique. For most atomization techniques, the slurry does not leave the atomizing mechanism as a final droplet 108, but rather as a fragment of a thin liquid film or ligament. The formation of droplets 108 takes place immediately after the liquid has left the atomizing mechanism, due to the surface tension of the liquid. The droplet size from a given type of atomization depends on the energy input into breaking the slurry into fragments, i.e., increasing the overall effective surface area of the slurry.

[0051] The average droplet size and distribution may be fairly constant for a given atomization technique, and may be in the range of 10 — 300 microns. The electrostatic charge process and resultant coulombic fission process in accordance with the various embodiments herein produces, in general, larger particles than conventional spray drying processes. The larger particles, however, come from even larger, parent particles, which conventional atomizers cannot adequately produce. The daughter particles produced in accordance with the embodiments herein are smaller, and the process tends to make bimodal size distributions for very viscous slurries.

[0052] Centrifugal (or rotary) atomization may be considered the most common form of atomization. Centrifugal atomization employs a rotating disc or wheel, which breaks the liquid stream of slurry into droplets. The centrifugal atomization device may employ a disc or wheel of about 5 to 50 cm in diameter, which spins in the range of about 5,000 to 40,000 rpm. The size of the droplets 108 produced by a centrifugal atomization device is about inversely proportional to the peripheral speed of the disc or wheel.

[0053] Nozzle atomization employs a pump (e.g., the feed pump 5 of FIG. 2), which pressurizes and forces the slurry through the orifice of a nozzle to break the liquid into fine

droplets. The orifice size is usually in the range of 0.5 to 30 mm. The size of the droplets depends on the size of the orifice and the pressure drop. A larger pressure drop across the orifice produces smaller droplets. Therefore, to reduce the particle/droplet size for a given feed rate, a smaller orifice and a higher pump pressure may be employed.

[0054] Two-fluid pneumatic atomization employs the interaction of the slurry with another fluid, usually compressed air using a fluid nozzle for the compressed air and a fluid nozzle for the slurry. The pressure of the air and slurry may be in the range of about 200 to 350 kPa. Particle size is controlled by varying a ratio of the compressed air flow to that of the slurry flow.

[0055] Sonic atomization employs ultrasonic energy to vibrate a surface at ultrasonic frequencies. The slurry is brought into contact with the vibrating surface in order to produce the particles/droplets 108.

[0056] With reference to FIGS. 3-5, one or more embodiments of the present invention may employ a nozzle-type atomizer 106. FIG. 3 is a cross-sectional view of a two-fluid atomizer 200 that may be employed as the atomizer 106 in the system of FIG. 2 in order to produce the wet particles/droplets 108 from the slurry. FIG. 4 is a cross-sectional view of a distal end of the two-fluid atomizer 200 of FIG. 3, and FIG. 5 is a perspective, exploded view of certain components of the distal end of the two-fluid atomizer 200 of FIG. 4.

[0057] The two-fluid atomizer 200 includes a body 202 having a proximal end 204 and a distal end 206. A channel 208 extends through the body 202 and includes an inlet 210, generally near the proximal end 204 of the body 202, and an outlet 212, generally near the distal end 206 of the body 202. The channel 208 operates to convey a first of the two-fluids, i.e., the slurry, from the inlet 210 to the outlet 212.

[0058] The two-fluid atomizer 200 also includes at least one electrode 214 operating to contact the slurry and apply an electrostatic charge thereto, such that the two-fluid atomizer 200 operates to produce a plurality of electrostatically charged wet particles/droplets 108. In one or more embodiments, the at least one electrode 214 may be disposed within the body 202 of the two-fluid atomizer 200 such that the slurry contacts the electrode 214 and becomes electrostatically charged while flowing from the inlet 210 to the outlet 212 of the channel 208. As illustrated in FIG. 3, the electrode 214 may be disposed within the channel 208, preferably in a coaxial arrangement, such that a significant portion of the surface area of the electrode 214 is available for contact with the slurry. The electrode 214 may be inserted into the channel 208 by way of a threaded bore of the body 202 and complementary threaded shaft of the electrode 214, which when engaged, positions the electrode within the channel 208. A connection terminal 216 may be electrically and mechanically coupled to the electrode 214 in order to provide a means for

connecting with the high voltage supply 104 and receiving voltage potential at the surface of the electrode 214.

[0059] With reference to FIGS. 3 and 4, the two-fluid atomizer 200 may include a nozzle 220 in fluid communication with the outlet 212 of the channel 208. In particular, the outlet 212 of the channel 208 includes a tube 224 sized and shaped to engage, and be received within, a complementary bore 226 at an inlet end 228 of the nozzle 220. The engagement of the tube 224 and bore 226 permits fluid communication of the slurry (which has been electrostatically charged) from the channel 208 into an internal volume 230 intermediately disposed within the nozzle 220. A sealing ring 232 may be employed to ensure a fluid tight seal between the tube 224 and the bore 226, even under fluid pressure. The nozzle 220 preferably includes a transition section 234 of reducing diameter (a tapering surface) extending from the internal volume 230 to a nozzle orifice 236. The nozzle orifice 236 is preferably of a generally cylindrical shape, including an internal bore of a size sufficient to produce wet particles/droplets 108 of desired size and shape once they succumb to surface tension forces.

[0060] The two-fluid atomizer 200 may further include a nozzle cap 222, which generally surrounds the nozzle 220 and permits the nozzle orifice 236 to extend through a bore 266 at a distal end thereof. The nozzle cap 222 includes an engagement feature at a proximal end thereof, which engages the distal end of the body 202. In particular, the nozzle cap 222 includes a threaded shank 238, which threads into a complementary threaded bore 240 of the body 202. A sealing ring 242 may be employed to ensure a fluid tight seal as between an internal surface 244 of the nozzle cap 222 and an external surface 246 of the nozzle 220, thereby forming an internal volume 248 therebetween.

[0061] The two-fluid atomizer 200 includes another channel 250 extending through the body 202, which includes an inlet 252, generally near the proximal end 204 of the body 202, and an outlet 254, generally near the distal end 206 of the body 202. The channel 250 operates to convey a second of the two-fluids, i.e., the non-heated air, from the inlet 252 to the outlet 254. The outlet 254 is in fluid communication with the internal volume 248 (between the internal surface 244 of the nozzle cap 222 and the external surface 246 of the nozzle 220). Thus, the channel 250 operates to convey the non-heated air from the proximal end 204 to the distal end 206 of the two-fluid atomizer 200. The flow of the non-heated air through the two-fluid atomizer 200 may be about 5100 m^3/hr at an input pressure of about 130 psi.

[0062] As best seen in FIGS. 4-5, the nozzle 220 includes a tapered surface 260 on an exterior thereof, which is downstream of the exterior surface 246 and downstream of the internal volume 248. The nozzle cap 222 includes a complementary internal surface in abutment with the

tapered surface 260. A number of grooves (recesses) 262 are disposed in the tapered surface 260 and extend from the internal volume 248 toward the nozzle orifice 236. When the complementary internal surface of the nozzle cap 222 is in abutment with the tapered surface 260, the grooves 262 provide fluid communication of the non-heated air from the internal volume 248 toward the nozzle orifice 236. The grooves terminate at an annular space 264 between a peripheral edge of the tapered surface 260 and the outer surface of the nozzle orifice 236, where the nozzle orifice 236 exits the nozzle 220. The annular space 264 is in fluid communication with the bore 266, whereby a suitably sized bore (larger than a diameter of the nozzle orifice 236) permits the non-heated air to exit the nozzle 220 and nozzle cap 222 under pressure. Preferably, the grooves 262 extend such that they terminate tangentially to the annular space 264 and thereby cause the non-heated air to produce a swirling fluid motion within the space 264 and in the vicinity of the nozzle orifice 236 after it has exited the bore 266.

[0063] The swirling fluid motion of the non-heated air, as it leaves the nozzle 220 and nozzle cap 222, imparts a swirling agitation to the plurality of wet particles/droplets 108 as they leave the nozzle 220. Such swirling agitation may suspend and agitate the wet particles/droplets 108 in order to achieve the aforementioned fission and evaporation. The above approach to atomization enables relatively high slurry throughput, on the order of 1-20 kg/hr at an input pressure of about 20 - 100 psi.

[0064] Reference is now made to FIG. 6, which is a schematic, side view of a drying chamber 107 that may be employed in the system 100 of FIG. 2 in accordance with one or more aspects of the present invention. The drying chamber 107 may include an inlet end 300, an outlet end 302, and an internal volume 304, within which the wet particles/droplets 108 are dried. The drying chamber is formed from a non-electrically conductive material. It is noted that the choice of materials (in this case a non-electrically conductive material, a non-metal) is not a mere matter of obvious design choice. Indeed, the conventional wisdom of the prior art spray drying process requires heated air (on the order of 200 °C), which consequently requires a metal drying chamber (typically stainless steel), otherwise the chamber would warp or otherwise fail.

[0065] A benefit of using non-heated air (which is directly counter to the conventional wisdom in the spray drying art) is that the drying chamber 107 may be formed from a non-metallic material; indeed, the temperature inside the drying chamber 107 may be less than 50 °C. Thus, materials such as polymer-based composites may be employed for implementing the basic drying chamber 107. By way of example, filament wound fiberglass composite tanks (which are used for storage of water, various food stuffs, grain storage, brines and many non-food based applications) have excellent load carrying properties and can be used for making very large tanks.

In one or more embodiments, such filament wound fiberglass composite materials may be used to fabricate the drying chamber 107 discussed herein. An advantage of using engineered plastics is the lower cost of the basic materials and the cost of manufacturing when compared to similar sized vessels made from stainless steel, for example. These materials also enable greater flexibility in the design of the drying chamber 107, making complex shapes possible, which are much more difficult and expensive to manufacture from stainless steel.

[0066] The use of non-metallic, non-conducting dielectric materials to form the drying chamber 107 (such as the engineered plastic composite materials), permits the use of one or more electric fields within the drying chamber 107 itself, to urge the particles/droplets 108 into desired trajectories and/or to urge such particles/droplets 108 from the inlet end 300 toward the outlet end 302 of the drying chamber 107. Notably, it is virtually impossible to develop an electric field inside a metallic, conductive vessel of the prior art because all charge accumulates on the surface of the vessel.

[0067] In accordance with one or more embodiments, the drying chamber 107 may include a first electrode 310 located at or near the inlet end 300 thereof, and a second electrode 312 located at or near the outlet end 302 of the drying chamber 107. The application of a source of voltage potential between the first and second electrodes 310, 312 induces an electric field (illustrated as broken lines) within the drying chamber 107 sufficient to urge the particles/droplets 108 into desired trajectories as they dry within the chamber 107. One such desirable trajectory is to cause the lines of the electric field to extend generally parallel to the walls of the drying chamber 107, even where such walls taper toward the outlet end 302. To achieve such trajectory, the second electrode 312 would have to be of a relatively small diameter as compared to the first electrode 310 (as is depicted by only the solid portion of the line of the electrode 312.) If the first and second electrodes 310, 312 are of generally the same diameter, then the lines of the electric field would extend generally parallel to the walls of the drying chamber 107, and then pass through the tapered walls at the outlet end 302. Other particle trajectories may be achieved based on number, location, size, and shape of the electrodes. As illustrated, the first and second electrodes 310, 312 may be disposed external to the drying chamber 107, yet induce an electric field within the internal volume 304 of the drying chamber 107 by virtue of the formation thereof from non-electrically conductive material.

[0068] To illustrate the utility of the no heat spray drying process for probiotic applications, Dannon™ Aunatural plain yogurt was subject to spray drying process described herein. In order to show that the bacteria (called L.acidophilus) survived the process, the spray dried yogurt was used to produce a new culture of yogurt. Since yogurt is approximately 85% water by weight, a

slurry was formed using 643 grams of starch M180 and 357 grams of yogurt to make a 1 kg batch of slurry. The starch to yogurt ratio was about 1.8. The slurry was subject to the no-heat drying process discussed above with respect to FIG. 2 and related illustrations. The resulting powder was then mixed with milk and a new yogurt culture was produced. A control culture using some of the original yogurt was also made. The spray dried bacteria produced the same amount of culture as the control using comparable starting weights of bacteria.

[0069] Reference is now made to FIGS. 7-8, which respectively are an image of dried powder non-fibrous particles produced using the system of FIG. 2, and a cross-section through one of the dried powder particles of FIG. 7. As can be seen in the scanning electron images, the dried particle morphology benefits from a no-heat process in that the particles do not experience an abrupt rise in temperature as they enter the drying chamber and the particles do not exhibit cracks on the surface, volcano structures on the surface, or hollow regions within the particles. The cross-section of the particle shows a uniform distribution of encapsulated constituent component(s), in this case flavor oil droplets, in the micron-diameter range.

[0070] Reference is now made to FIGS. 9-10, which respectively are scanning electron images of dried powder fibers produced using the system of FIG. 2, and a cross-section through one of the dried powder fibers. Through modifications of the emulsion of the slurry, it is also possible to produce fibers instead of particles. For example, to make fibers one may change the carrier material (e.g., the starch) to a lower DE (dextrose equivalent), such that the concentration level at which an "entanglement transition" occurs is crossed. At such concentration level, the large starch molecules interact in a manner such that the slurry begins to manifest extensional viscoelastic properties that permit fibers to form. As can be seen in the scanning electron images, the dried fiber morphology is also characterized by a lack of cracks on the surface, volcano structures on the surface, or hollow regions within the fibers. The cross-section of the fiber also shows a uniform distribution of encapsulated constituent component(s), in this case flavor oil droplets, in the micron-diameter range.

[0071] Reference is now made to FIG. 11, which is a graph illustrating the weight percentage of the desired component(s) within dried powder particles produced using the system of FIG. 2 as compared with the conventional spray drying process. The no-heat process has demonstrated higher levels of preservation of starting active ingredients such as volatile flavor molecules. FIG. 11 shows the results of a 1000 hour accelerated aging study (at elevated temperatures of about 95 °F) comparing powders produced by conventional spray dry processing and the no-heat process. In the illustrated results, amounts of a particular constituent component, in this case a principle molecular type called D-Limonene (obtained from orange oil), were

measured in an un-processed source of flavor oil 400, dried powder 402 produced in accordance with the no-heat process described herein, and dried powder 404 produced in accordance with the prior art heated air process. As FIG. 11 clearly shows, the no-heat powder 402 retains essentially the same flavor oil composition as the original oil source 400 used to produce the starting slurry, whereas the conventionally spray dried powder 404 departs significantly from the original starting oil 400. Similar results were found for all other principal constituents of other flavor oils. Additionally, the appearance of degradation products was greatly diminished in the no-heat samples, resulting in longer projected shelf-life of the powder.

[0072] The above data reveal that not only are some of the structures and processes of the system 100 of FIG. 2 inventive, but the dried powder (or fiber) itself is inventive. Indeed, the resultant dried powder (or fiber) includes a plurality of dried particles/fibers, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying the slurry, which contained an initial active ingredient, a liquid solvent and the carrier. The initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, bacteria, probiotic, pigment, etc. is obtained. The final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry. A weight percentage of at least one of the one or more principle molecular types in the final active ingredient is essentially the same (e.g., within about 5%, 4%, 3%, or 1% of a) weight percentage of the corresponding principle molecular types in the initial active ingredient.

[0073] Another way to characterize the inventive characteristics of the dried powder/fibers is that a weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary significantly (not by more than about 5%, 4%, 3%, 2%, or 1%) during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

[0074] The present disclosure provides a new method of spray drying, using a low temperature, e.g., "no heat", spray drying process that produces powder products with superior flavor retention and stability. The spray drying method of the present disclosure does not employ purposely heated gas for removing water from the atomized fluid droplets, as has been the case in previously employed spray drying operations. The spray drying method of the present disclosure instead uses unheated air, e.g., dehumidified air, to carry out high throughput atomization processes, utilizing unique dryer designs and high solids content (low water content) slurries/emulsions with extremely high viscosities (for example, viscosities in a range of from 500

to 10000 mPa-s) to produce powders dried at low temperatures, such as temperatures on the order of from 5 to 50°C.

[0075] In specific embodiments, the air utilized in the spray drying operation may have a relative humidity of 10% or less, e.g., less than 8%, 7%, 6%, 5%, 4%, 3%, 2%, or 1%. The dewpoint of such air may be in a range of from -20°C to 5°C, such as in a range of from -15°C to 5°C, from -12°C to 3°C, from -12°C to 0°C, from -12°C to -5°C, or any other suitable dewpoint range appropriate to the spray drying operation.

[0076] The use of high solids content emulsions (with solids concentrations of at least 40% by weight, based on total weight of the emulsion, and preferably at least 50% by weight on the same total weight basis) in the low temperature, e.g., no heat, spray drying process of the present disclosure provides a host of desirable attributes to the final powders produced by the process, such as: (1) high particle density, with density greater than that of water (i.e., > 1 g/cc), so that the particles readily sink into aqueous solution and become rapidly dissolved or suspended, (2) greater resistance to oxidation imparted by the higher solids content, (3) substantial energy efficiency from the use of high solids content slurries/emulsions coupled with low temperatures, since about half as much water is evaporated as compared to traditional spray drying processes, and (4) superior retention of high value active ingredients such as flavors or fragrances, as another substantial economic advantage brought about by low temperature drying and high solids content slurries/emulsions.

[0077] By contrast, conventional high temperature drying processes lose a significant amount of the highly volatile flavor or fragrance active constituents to evaporation and oxidation, resulting in powders with less desirable flavor and aroma attributes. These powders resulting from high temperature conventional processes are typically of small average diameter, e.g., on the order of 60 -100 micrometers, are not fully dense, and are difficult to dissolve in aqueous solutions. Powders produced by the low temperature spray drying process of the present disclosure, by contrast, have large average diameters, such as on the order of 125 – 250 micrometers, are fully dense, and readily go into solution.

[0078] The spray drying process of the present disclosure as a consequence of its low temperature, e.g., no heat, character, may be utilized for preparation of spray dried products that contain highly volatile components, e.g., volatile active ingredients whose boiling points are less than 100°C, and may for example be less than 90°C, 80°C, 70°C, 65°C, 60°C, 55°C, 50°C, 45°C, 40°C, 35°C, or even lower.

[0079] The spray drying process of the present disclosure may be employed to form spray dried powders and fibers in which one or more of the principle molecular types include aldehydes

such as acetaldehydes, valeraldehyde, iso-valeraldehyde, etc., dimethyl and other alkyl sulfides, acetates such as ethyl acetates and other alkyl acetates, proprionates such as ethyl proprionate, alkyl butyrates such as methyl butyrate and ethyl butyrate, ketones, esters, etc.

[0080] Spray dried powders and fibers of the present disclosure, wherein volatile active ingredient(s) are highly retained, may be incorporated into any suitable products, such as for example beverages, sports beverages, nutritional beverages, gums, dairy products, soups, sauces, condiments, baked goods, personal-care products, oral care products, detergents, fresheners, etc.

[0081] Spray dried powders and fibers of the present disclosure thus can be produced in which the final active ingredient includes one or more of the constituent components corresponding to those of the initial active ingredient as modified by the spray drying process, wherein the spray dried powder or fiber composition has at least one of the characteristics of (i) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient which is within about 15% of a weight percentage of the corresponding principle molecular types in the initial active ingredient, and which may for example be within about 12%, 10%, 8%, 7%, 6%, 5%, 4%, 3%, 2% or 1% of the weight percentage of the corresponding principle molecular types in the initial active ingredient, and (ii) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient which does not vary by more than about 15% during aging of the dried powder or fiber during any period of elevated temperature of about 95°F up to about 1000 hours, and which may for example not vary by more than about 12%, 10%, 8%, 7%, 6%, 5%, 4%, 3%, 2% or 1% during such aging.

[0082] The present disclosure thus embodies a novel approach for slurry or emulsion formulation for use in a low/no heat spray drying process, resulting in greatly improved powder properties and sensory characteristics of taste, aroma, etc.

[0083] In addition to having broad utility for processing of a wide variety of natural and artificial products, the spray drying process of the present disclosure is useful in the context of increasing utilization of natural products, including the proliferating use of essential oils extracted from natural sources. Essential oils are composed of wide ranges of lipophilic and highly volatile components covering a diverse spectrum of chemical classes. Essential oils, however, are susceptible to conversion and degradation reactions. Heat and light exposure and oxygen availability can significantly impact essential oil integrity. The low temperature spray drying process of the present disclosure substantially mitigates the degrading effects of heat and oxidation on the encapsulated flavor oil, as is illustrated in the following examples.

[0084] EXAMPLE 1

[0085] D-limonene Assessment

[0086] In order to demonstrate some of the important advantages of the "no heat" spray dry process over traditional spray dry processing, flavor powders prepared by both methods were subjected to an accelerated aging test. The test powders were placed into an oven maintained at a temperature of 95° Fahrenheit. Once every seven days a sample of each powder was analyzed via gas chromatography mass spectrometry (GC-MS) analysis to determine the presence or absence of key molecular constituents. The flavor oil for analysis was extracted from the powder samples using standard procedures.

[0087] The results for both conventionally spray dried and no heat spray dried powders were also compared to a control sample of the starting neat flavor oil ("Neat Oil") subjected to the same storage conditions as the powders. The test was run for a period of 9 weeks. This test simulates degradation processes that a powder will experience over its shelf life. The primary degradation processes are oxidation of key flavor molecules, with the oxidation products being the cause of spoilage and development of "off" taste in the product. The GC-MS comparison also reveals deficits in key flavor constituents due to evaporation that occurred during the spray dry processing as compared to the starting flavor oil control sample.

[0088] In this study a lemon-lime flavor oil was selected because it is highly representative of the key volatile essential oil flavor molecules (top notes) that are present in a wide range of citrus based flavors. These key flavor molecules are highly susceptible to oxidation, have low boiling points, and are easily evaporated.

[0089] The emulsions for both samples contained a 10% by weight load of the lemon-lime flavor oil. Both emulsions used a carrier starch and emulsifier. The spray drying emulsion in accordance with the present disclosure (Sample A, "Zoom") contained 30% water, 6% starch emulsifier, and the remainder was 54% starch (all percentages by weight, based on total weight of the composition) and was spray dried at an inlet air temperature of 42°C. The sample for traditional spray dry processing (Sample B, "Spray") was produced by Adron, Inc., (94 Fanny Rd, Boonton, NJ 07005, USA), using the same lot of lemon lime flavor oil.

[0090] The most abundant and readily perceived molecule in citrus flavors is d-limonene. D-limonene is a volatile top note component, which adds to the fresh, light, lemon, orange, and sweet citrus notes in the flavor. A decrease of d-limonene concentration in the citrus flavor composition dramatically alters the citrus flavor in an undesirable manner. When citrus oils spoil it is primarily due to oxidation of d-limonene. Oxidation decreases the d-limonene concentration, thereby giving rise to various unwanted oxidation products, such as p-cymene, p-cymene-8ol, epoxides, menthadienols, and gamma-terpinene.

[0091] FIG. 12 compares the mass spectrometric results for d-limonene content in the control neat lemon-lime oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"). In FIG. 12, d-limonene content is plotted as a function of time of exposure to hot air at a temperature of 95°F, over a period of 9 weeks. The traditional spray dry powder ("Spray") exhibited severe degradation of d-limonene, as compared to the control neat oil ("Neat Oil") and the low temperature dried powder of the present disclosure ("Zoom").

[0092] These results illustrate two important findings. First, the concentration of d-limonene in the traditional spray dried powder was lower than the control and the Zoom dried samples from the outset, reflecting the occurrence of evaporation that takes place during the traditional spray drying process due to the presence of heat as the powder is made. Second, as time progressed, the concentration of d-limonene continued to decrease in the traditionally spray dried sample, while the control neat oil and Zoom dried samples did not show any significant degradation.

[0093] EXAMPLE 2

[0094] Gamma-Terpinene Assessment

[0095] Gamma-terpinene is normally present in lemon and lime oils, and contributes to the top note of the flavor. When gamma-terpinene oxidizes the principal oxidation product is para-cymene (p-cymene). The concentration of gamma-terpinene as a function of time is shown in FIG. 13, for the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"). FIG. 13 shows a comparison of the gamma-terpinene content as a function of time of exposure to hot air at a temperature of 95°F. There was a relatively fast decrease in gamma-terpinene concentration in the traditional spray dried powder within the first two weeks of testing. The control neat oil and Zoom dried powder showed a slight decrease over the 9 week period.

[0096] FIG. 14 is a comparison of para-cymene oxidation product for corresponding samples of the he control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"). The increased presence of p-cymene as seen in FIG. 14 is an indication of ongoing oxidation reactions. The presence of p-cymene produces an off-bitter tasting profile. As FIGS. 13 and 14 indicate, in the traditional spray dry powder, the gamma-terpinene concentration decreased just as quickly as the p-cymene concentration was increasing, reflecting a faster rate of oxidation in comparison to the Zoom dried powder and the control neat oil.

[0097] EXAMPLE 3

[0098] Alpha/Gamma Terpineol Assessment

[0099] Terpineols are a small constituent of citrus oils, which contribute to heavier, less fresh tastes. It is well known that alpha and gamma terpineols can be produced from limonene. The increased presence of alpha and gamma terpineol indicate ongoing oxidation processes.

[00100] FIG. 15 shows the concentration of alpha and gamma terpineols as a function of time, for the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"). FIG. 15 shows a comparison of the alpha and gamma terpineols content as a function of time of exposure to hot air at a temperature of 95°F. There was a large initial rise in the concentration of terpineols in the powder made by the traditional spray dry process. The concentration of terpineols in the Zoom dried powder and in the control neat oil sample remained constant over the course of the test indicating very low or nonexistent terpineol production.

[00101] EXAMPLE 4

[00102] Limonene/Terpinolene Epoxide Formation and P-Menthadienol Formation

[00103] The formation of limonene and terpinolene epoxides and p-menthadienol are the result of oxidation processes. These unwanted byproducts form far more rapidly in traditional spray dry powders than in the control neat oil or the Zoom dried powder, as shown by the results in FIG. 16.

[00104] FIG. 16 shows the concentration of limonene and terpinolene epoxide as a function of time, for the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"). FIG. 16 shows a comparison of the limonene and terpinolene epoxide content as a function of time of exposure to hot air at a temperature of 95°F. The epoxide concentration increased rapidly over the first 5 weeks, indicating a more rapid rate of oxidation in the traditionally spray dried powder.

[00105] Similar results are shown in FIG. 17 in the concentration of p-menthadienol , for the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"), as a function of time of exposure to hot air at a temperature of 95°F. The data show a continuing rise in the concentration of p-menthadienol in the traditionally spray dried sample.

[00106] EXAMPLE 5

[00107] Trans- and Cis-Carveol Assessment

[00108] Trans- and cis- carveol are also formed as a result of oxidation of limonene. Their concentration in the neat oil is very low. When the concentration of these constituents becomes too high in a citrus oil, it indicates the occurrence of spoilage, and results in an off-taste.

[00109] FIG. 18 shows the concentration of trans- and cis- carveol, for the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"), as a function of time of exposure to hot air at a temperature of 95°F. The data show that trans- and cis-carveol form at a much more rapid rate in the traditional spray dried powder than in either the control neat oil or in the Zoom dried powder.

[00110] EXAMPLE 6

[00111] P-Cymeme-8-ol Assessment

[00112] This assessment involved the determination of the oxidation product p-cymene-8-ol in the control neat oil ("Neat Oil"), the traditional spray dried powder (Sample B, "Spray") and the low temperature spray dried powder in accordance with present disclosure (Sample A, "Zoom"), as a function of time of exposure to hot air at a temperature of 95°F.

[00113] The results are shown in FIG. 19, as a graph of the concentration of p-cymene-8-ol, in weight percent, based on the weight of the sample, as a function of time for the 9 week assessment period. As shown by the data, the concentration of p-cymene-8-ol like p-cymene in the control neat oil was very low. Increases in concentration of p-cymene-8-ol are indicative of ongoing oxidation reaction. The increased formation of p-cymene-8-ol in the traditional spray dried powder when compared to the Zoom dried powder or the control neat oil, show that the spray dried sample was being oxidized faster than the Zoom dried sample, or the neat oil.

[00114] The foregoing empirical results show the substantially increased stability of spray dried products that is achievable by the "no heat" spray drying process of the present disclosure. These results show that such no heat spray drying process achieves extremely low loss of volatile flavor components that would otherwise occur as a result of evaporation and that the incidence of oxidative reactions in the spray dried powders of the present disclosure are greatly reduced, as compared with the levels that occur in traditional spray dried products. The spray dried powder products of the present disclosure retain dramatically higher levels of highly volatile and critical top note components of flavor oils. As a result, the shelf lives of spray dried powder products of the present disclosure greatly exceed those of traditional spray dried powder products.

THE CLAIMS

What is claimed is:

1. A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained;

the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry; and

a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

2. The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a food composition.

3. The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a flavor composition.

4. The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a fragrance composition.

5. The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a medicament composition.

6. The spray dried powder of claim 1, wherein the one or more principle molecular types are molecular types of a pigment composition.

7. The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 3% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

8. The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 2% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

9. The spray dried powder of claim 1, wherein the weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 1% of a weight percentage of the corresponding principle molecular types in the initial active ingredient.

10. A spray dried powder, comprising:

a plurality of dried particles, which individually contain an amount of active ingredient encapsulated within a carrier, wherein:

the active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

a weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 5% during aging of the dried powder during any period of elevated temperature of about 95 °F up to about 1000 hours.

11. The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a food composition.

12. The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a flavor composition.

13. The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a fragrance composition.

14. The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a medicament composition.

15. The spray dried powder of claim 10, wherein the one or more principle molecular types are molecular types of a pigment composition.

16. The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 3% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

17. The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 2% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

18. The spray dried powder of claim 10, wherein the weight percentage of at least one of the one or more principle molecular types in the active ingredient does not vary by more than about 1% during aging of the dried during any period of elevated temperature of about 95 °F up to about 1000 hours.

19. The spray dried powder of claim 10, wherein the carrier comprises starch.

20. A spray dried fiber composition, comprising:

a plurality of dried fibers, which individually contain an amount of final active ingredient encapsulated within a carrier resulting from drying a slurry containing an initial active ingredient, a liquid solvent and the carrier, wherein:

the initial active ingredient includes one or more constituent components, at least one of which is among one or more principle molecular types from which at least one of a desirable food, flavor, fragrance, medicament, and pigment is obtained; and

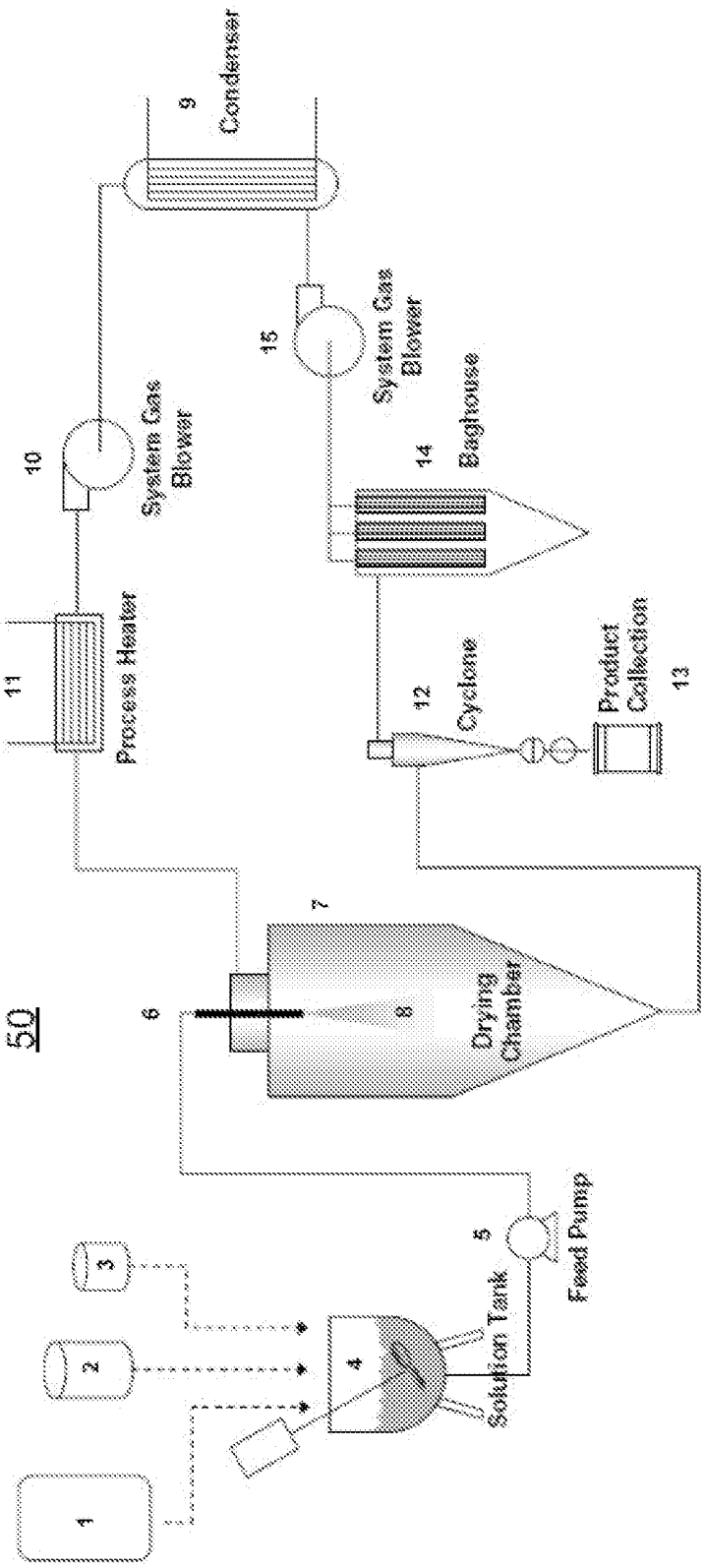
the final active ingredient includes one or more of the constituent components corresponding with those of the initial active ingredient as modified by the drying of the slurry, and wherein the spray dried fiber composition has at least one of the characteristics of (i) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient is within about 5% of a weight percentage of the corresponding principle molecular types in the initial active ingredient, and (ii) a weight percentage of at least one of the one or more principle molecular types in the final active ingredient does not vary by more than about 5%

during aging of the dried fibers during any period of elevated temperature of about 95°F up to about 1000 hours.

ABSTRACT

Methods and apparatus provide for spray drying a liquid product into a dried powder without applying heat, including: forming a slurry including a liquid solvent, a carrier, and an active ingredient; applying an electrostatic charge to the slurry; atomizing the charged slurry to produce a plurality of electrostatically charged, wet particles; suspending the electrostatically charged, wet particles for a sufficient time to permit repulsive forces induced by the electrostatic charge on at least some wet particles to cause at least some of such particles to divide into wet sub-particles; and continuing the suspending step, without the presence of any heated drying fluids, for a sufficient time to drive off a sufficient amount of the liquid solvent within most of the wet particles to leave a plurality of dried particles (the powder), each dried particle containing the active ingredient encapsulated within the carrier.

FIG. 1
(Prior Art)



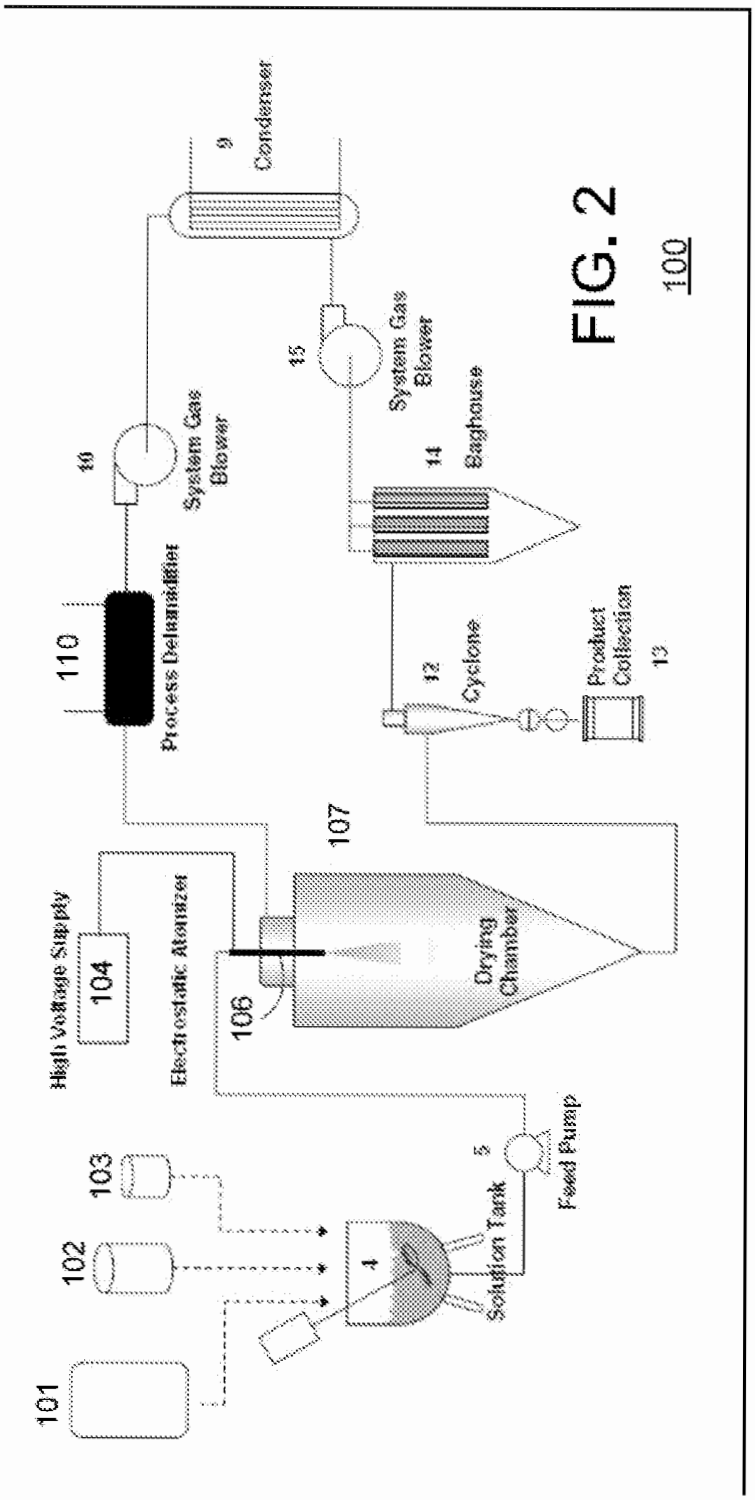
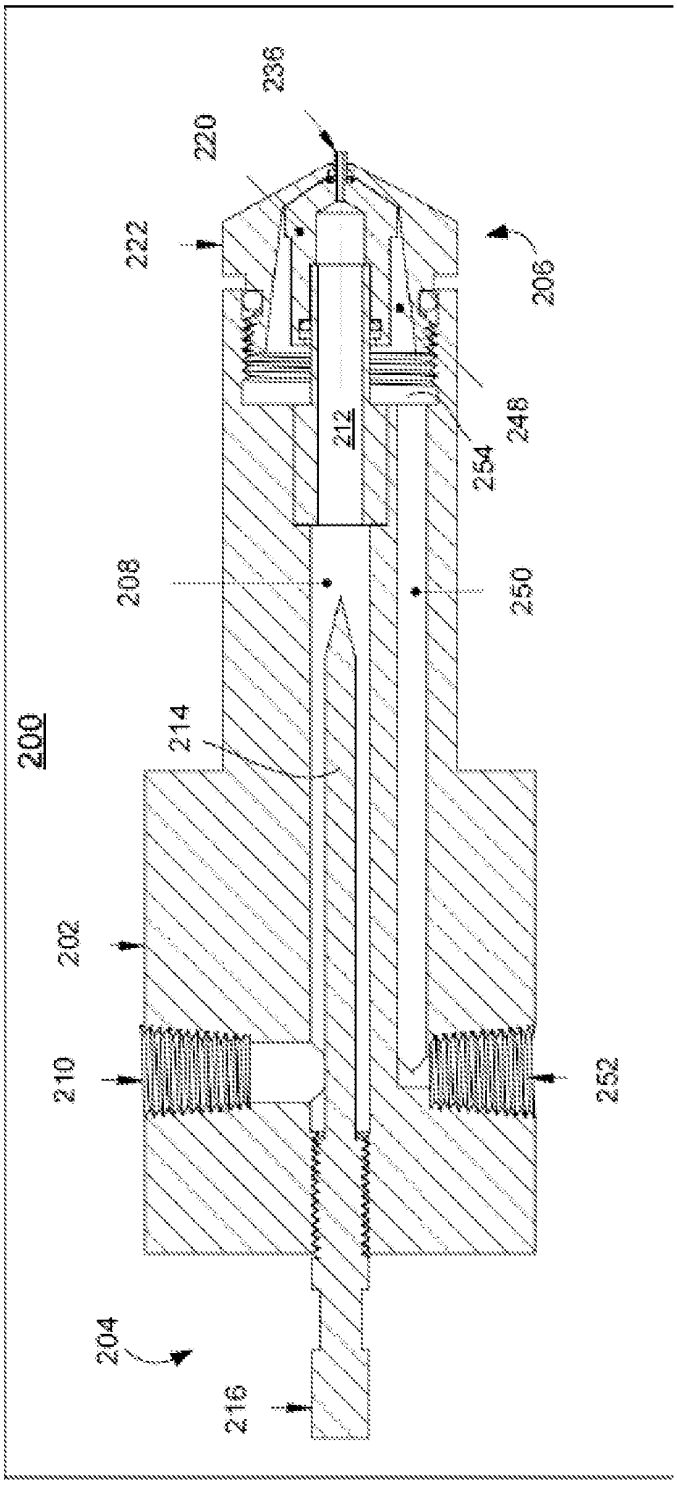

101
102
103
4
Solution Tank
5
Feed Pump
106
Electrostatic Atomizer
104
High Voltage Supply
107
Drying Chamber
12
Cyclone
13
Product Collection
110
Process Dehumidifier
10
System Gas Blower
9
Condenser
15
System Gas Blower
14
Baghouse
100

FIG. 2

FIG. 3



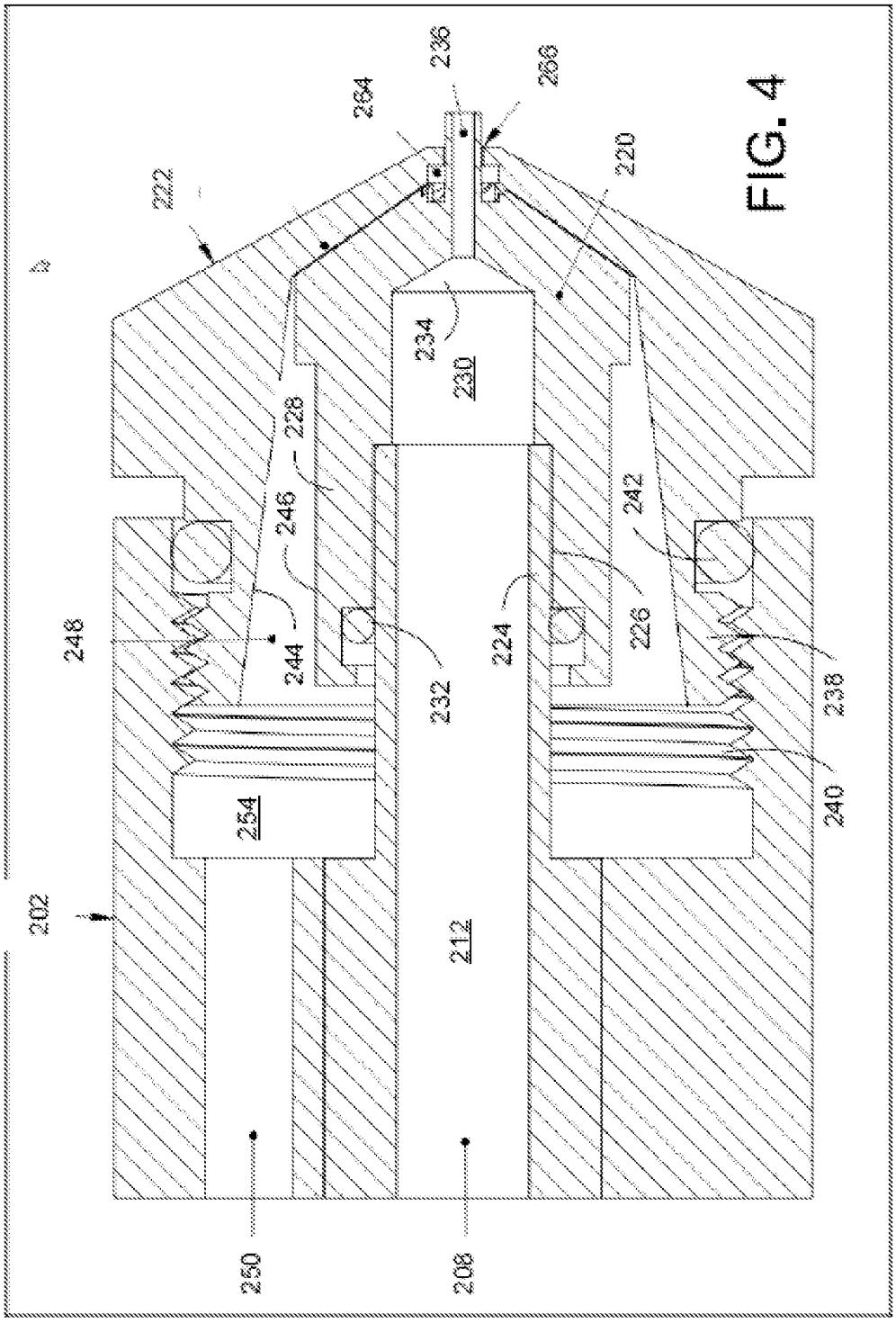

202
212
250
208
254
248
244
246
228
234
230
232
224
226
242
238
240
222
264
236
266
220

FIG. 4

FIG. 5

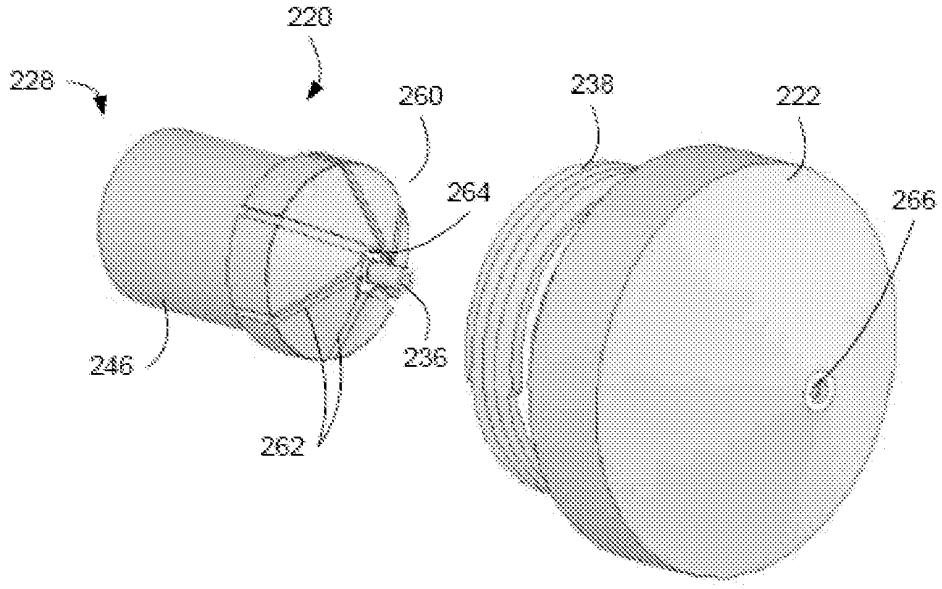


FIG. 6

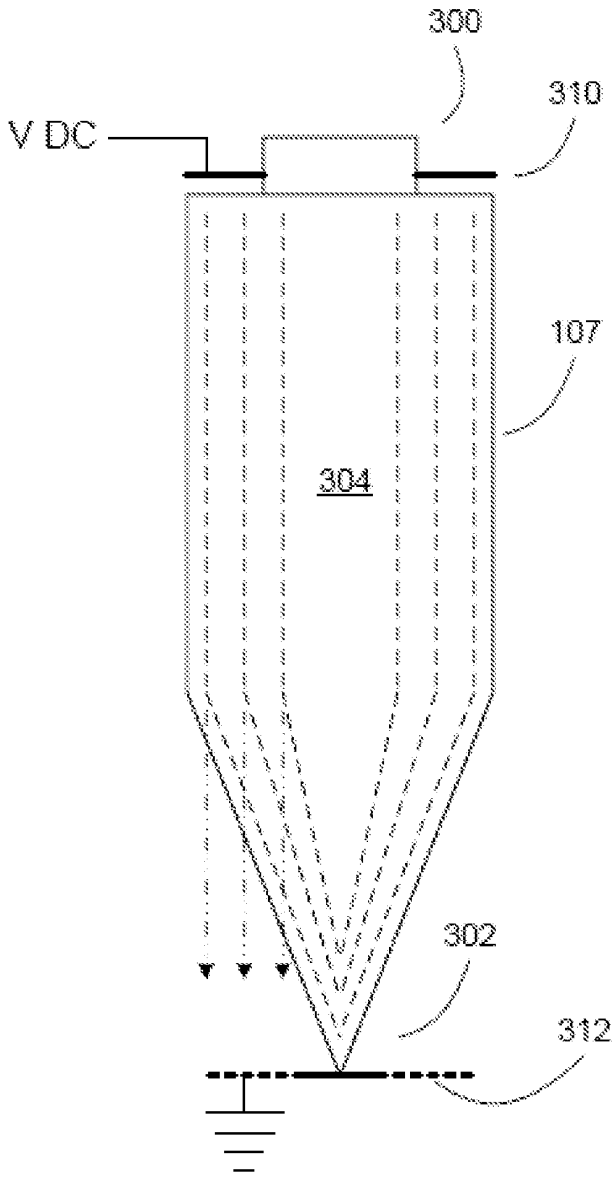


FIG. 7

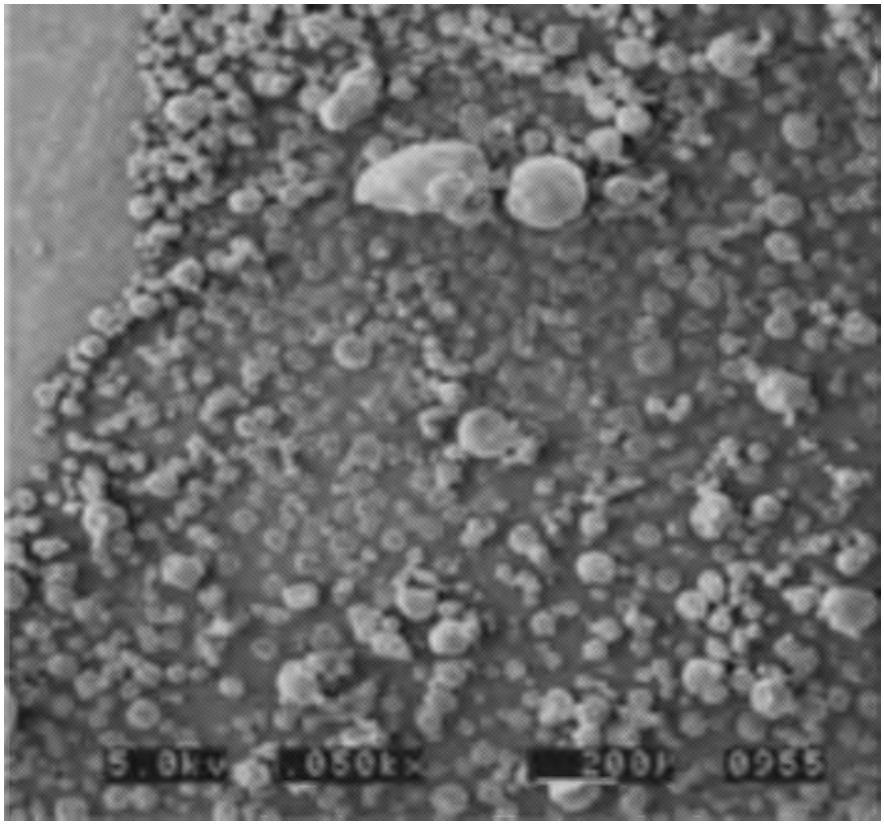


FIG. 8

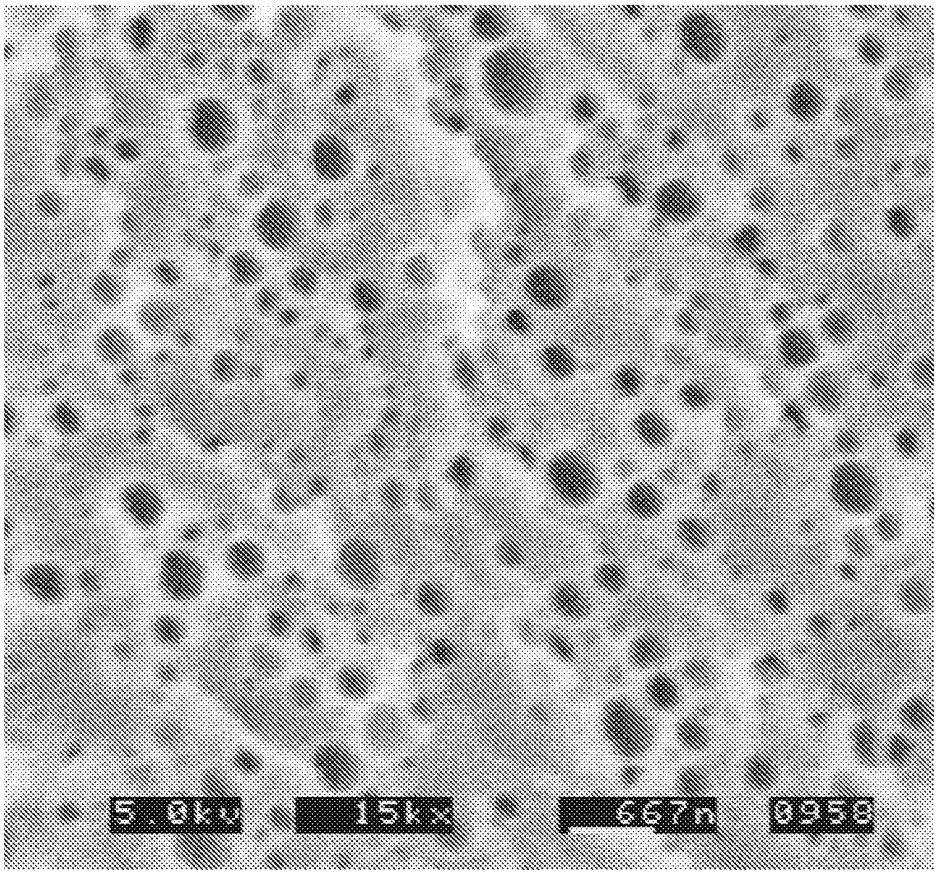


FIG. 9

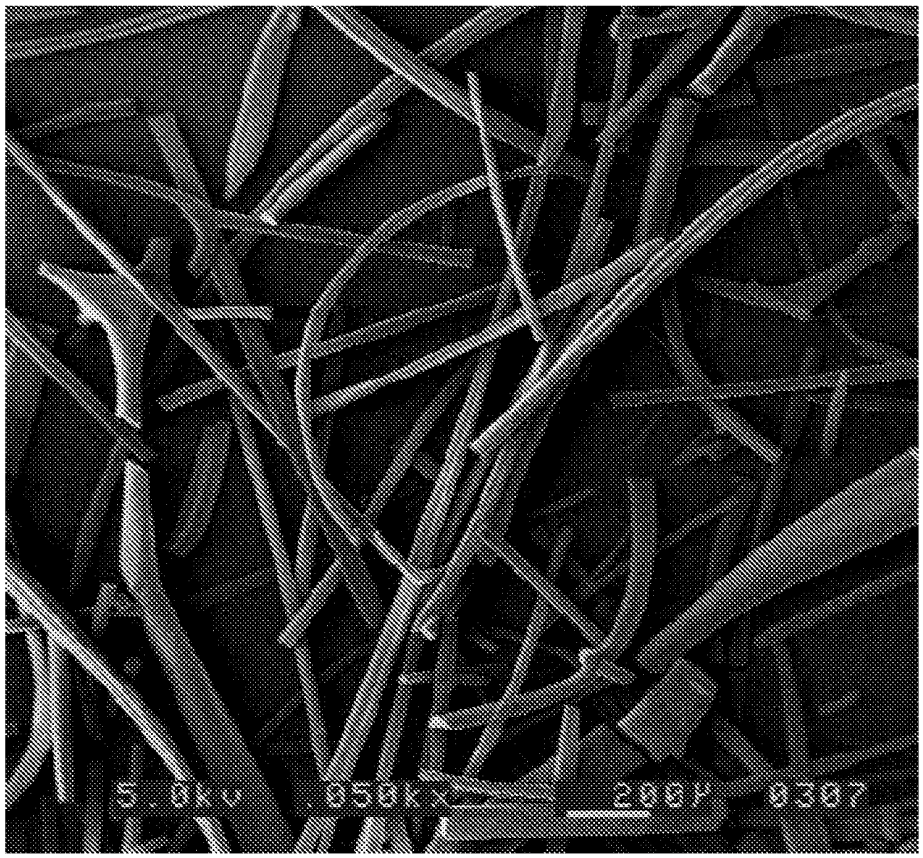


FIG. 10

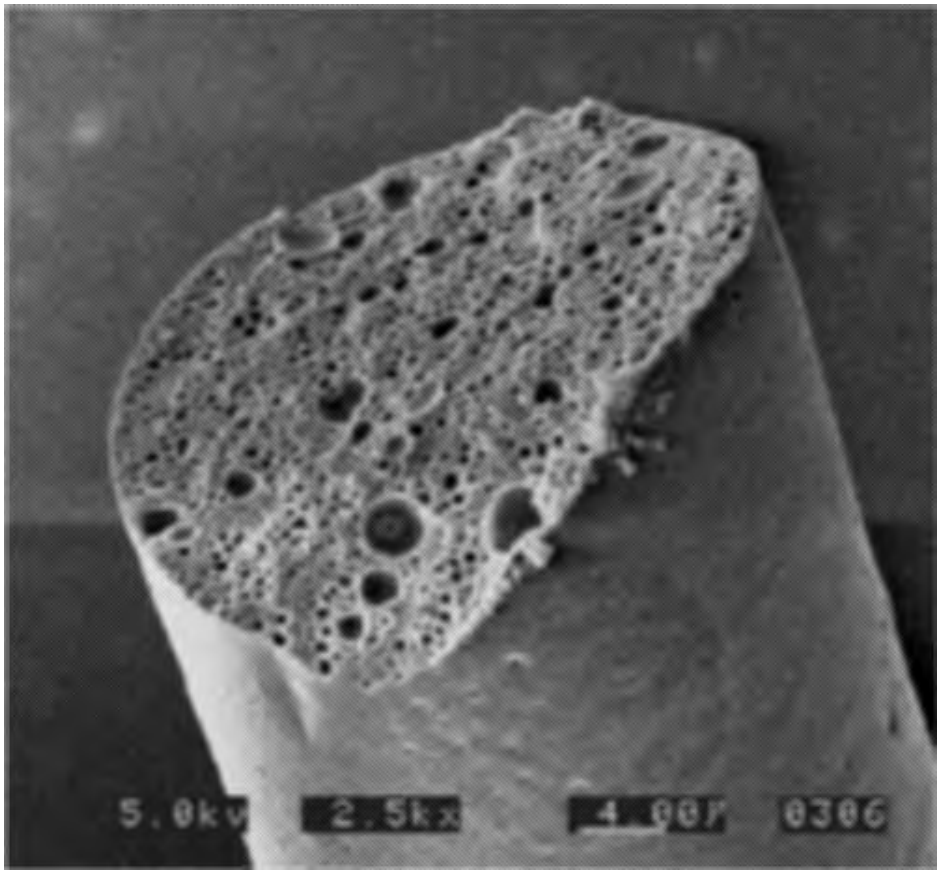


FIG. 11

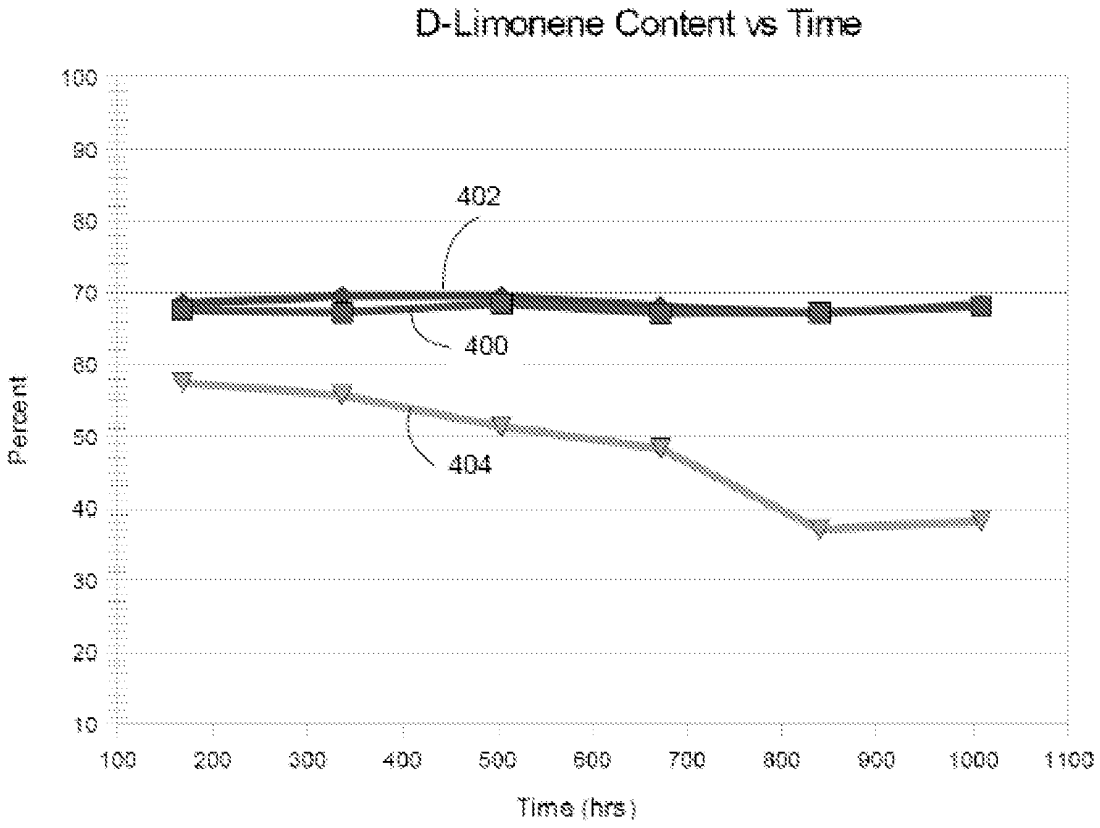

D-Limonene Content vs Time
Percent
100
90
80
70
60
50
40
30
20
10
100
200
300
400
500
600
700
800
900
1000
1100
Time (hrs)
402
400
404

FIG. 12

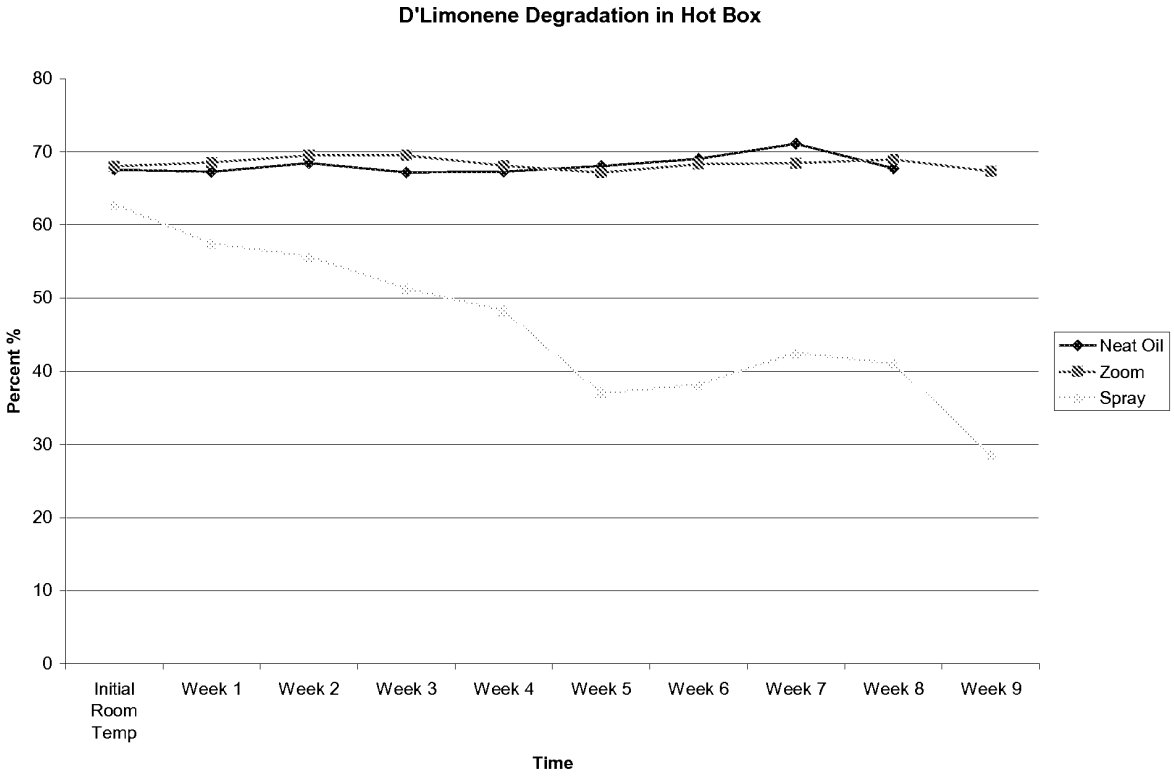

D'Limonene Degradation in Hot Box
Percent %
80
70
60
50
40
30
20
10
0
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 13

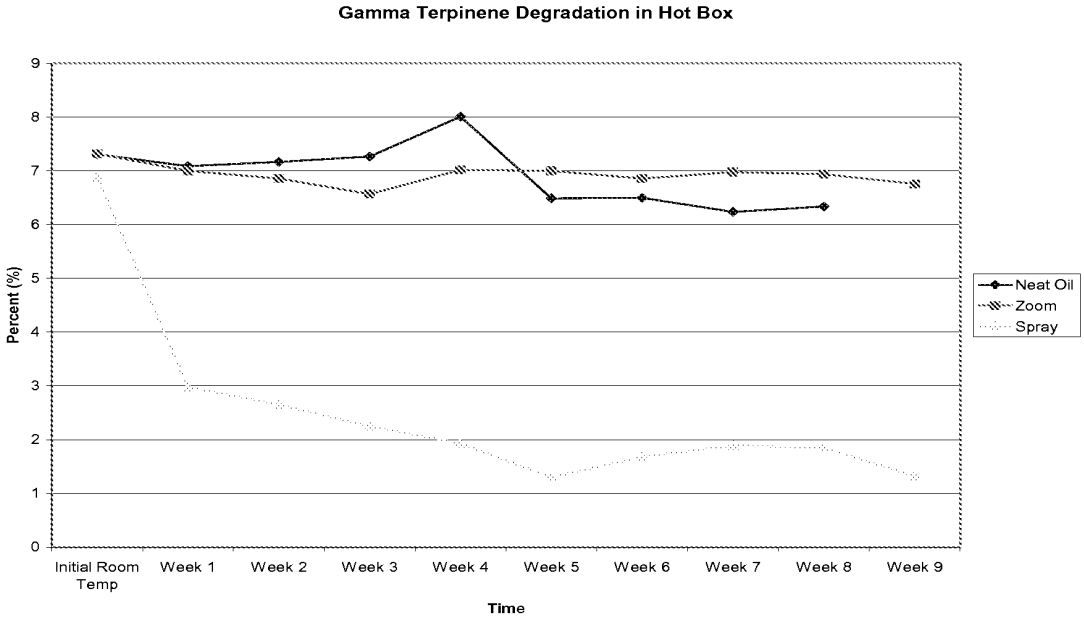

Gamma Terpinene Degradation in Hot Box
Percent (%)
0
1
2
3
4
5
6
7
8
9
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 14

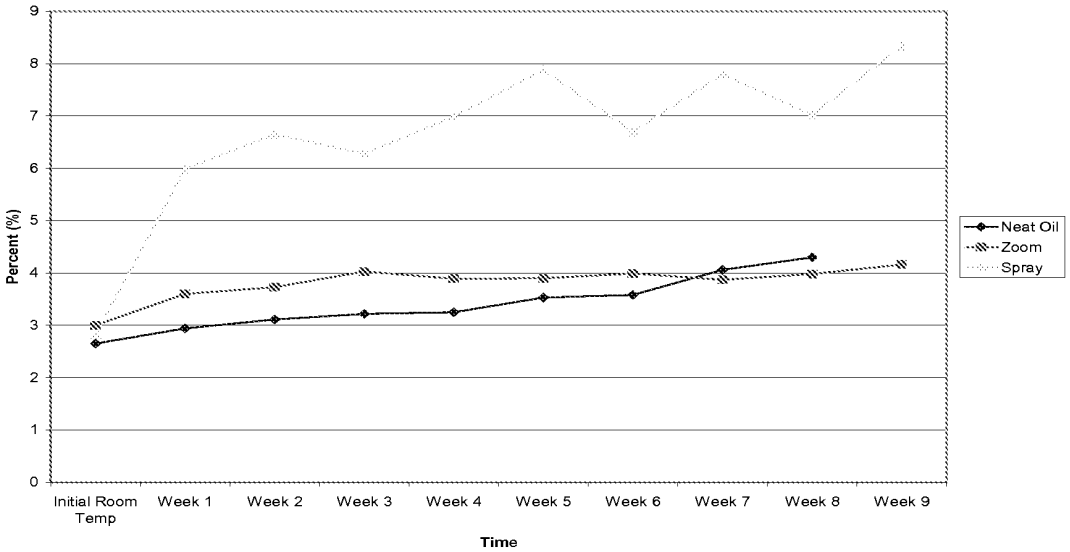

Para-Cymene Formation in Hot Box
Percent (%)
0
1
2
3
4
5
6
7
8
9
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 15

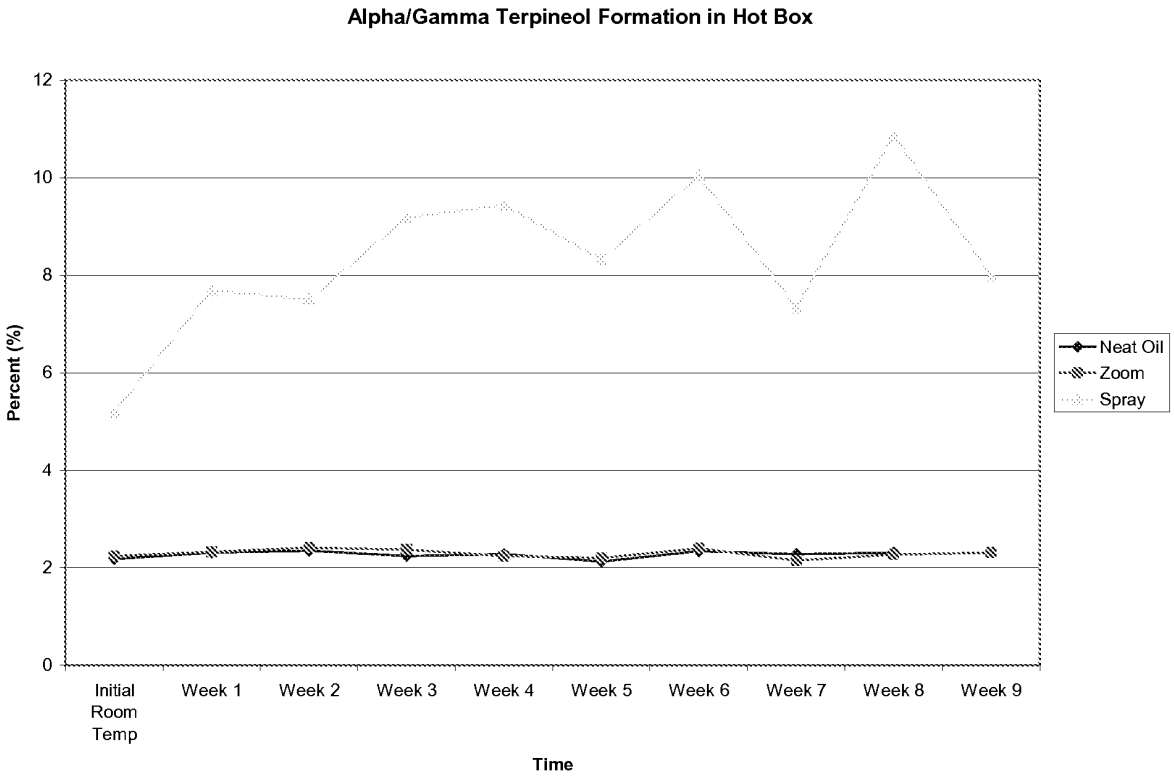

Alpha/Gamma Terpineol Formation in Hot Box
Percent (%)
0
2
4
6
8
10
12
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 16

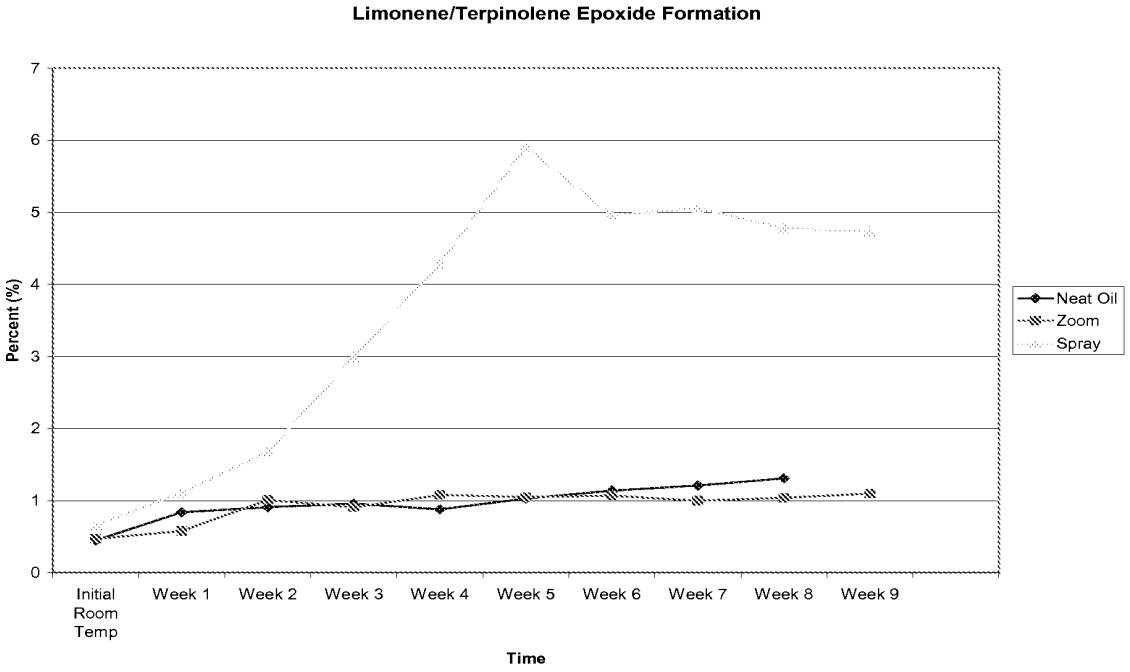

Limonene/Terpinolene Epoxide Formation
Percent (%)
0
1
2
3
4
5
6
7
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 17

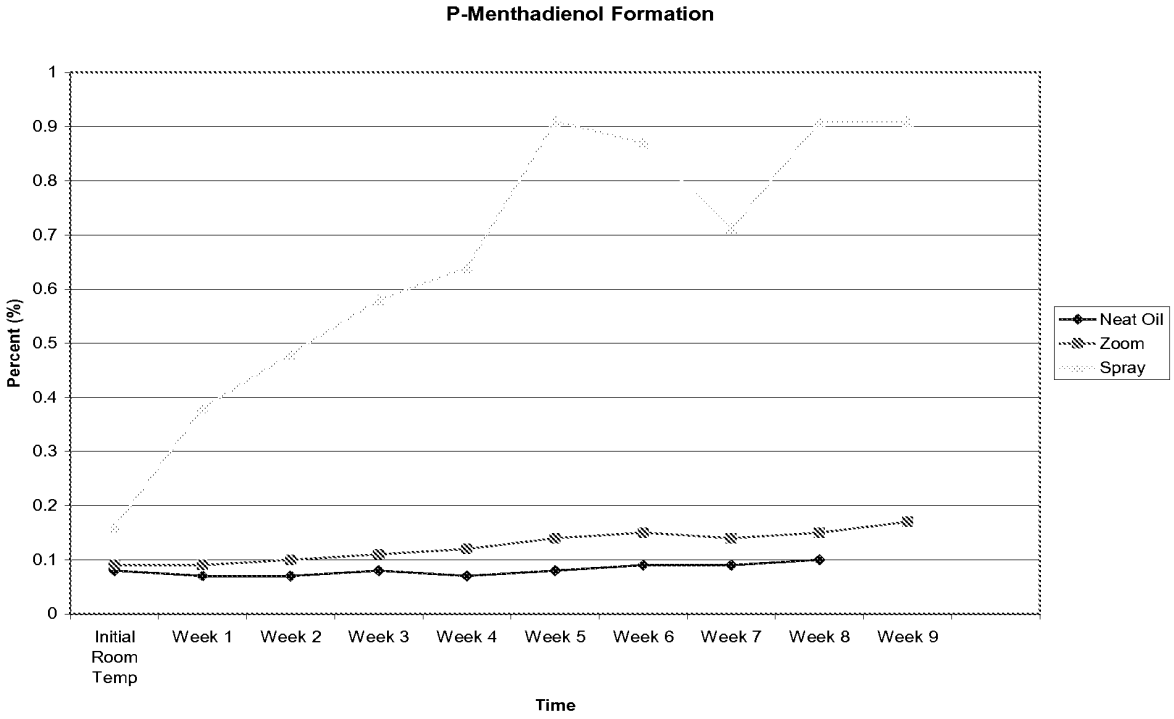

P-Menthadienol Formation
Percent (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 18

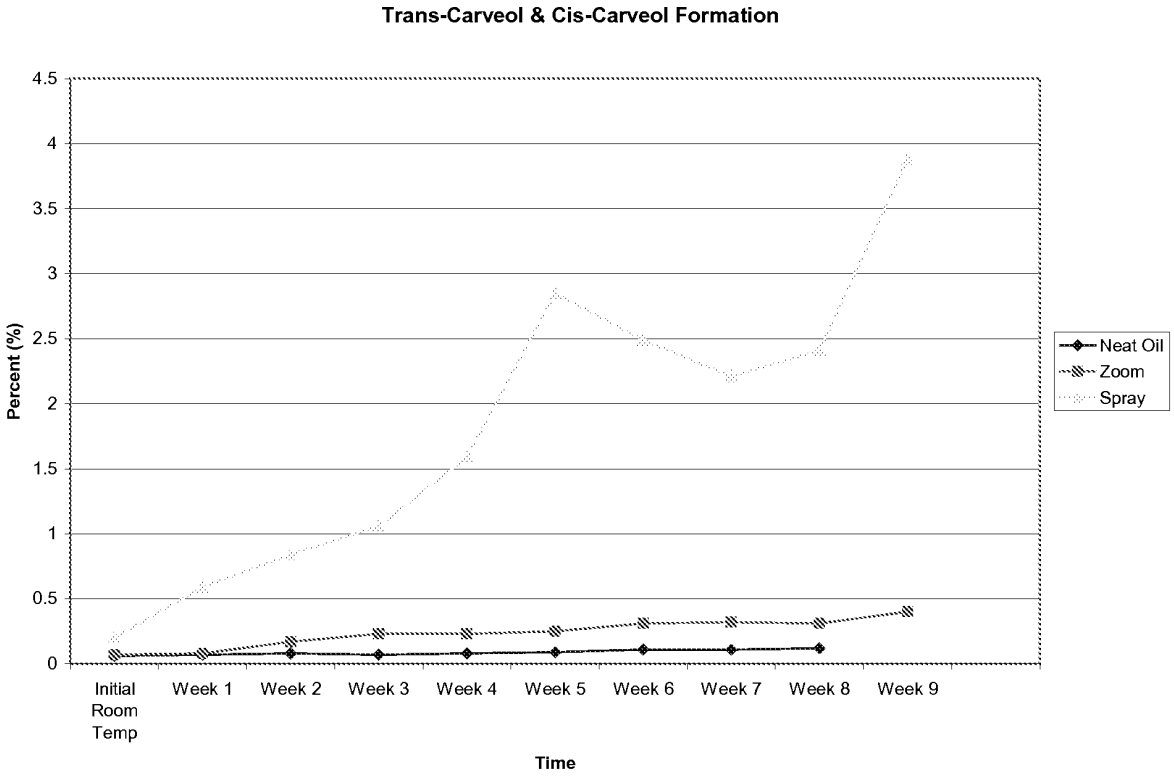
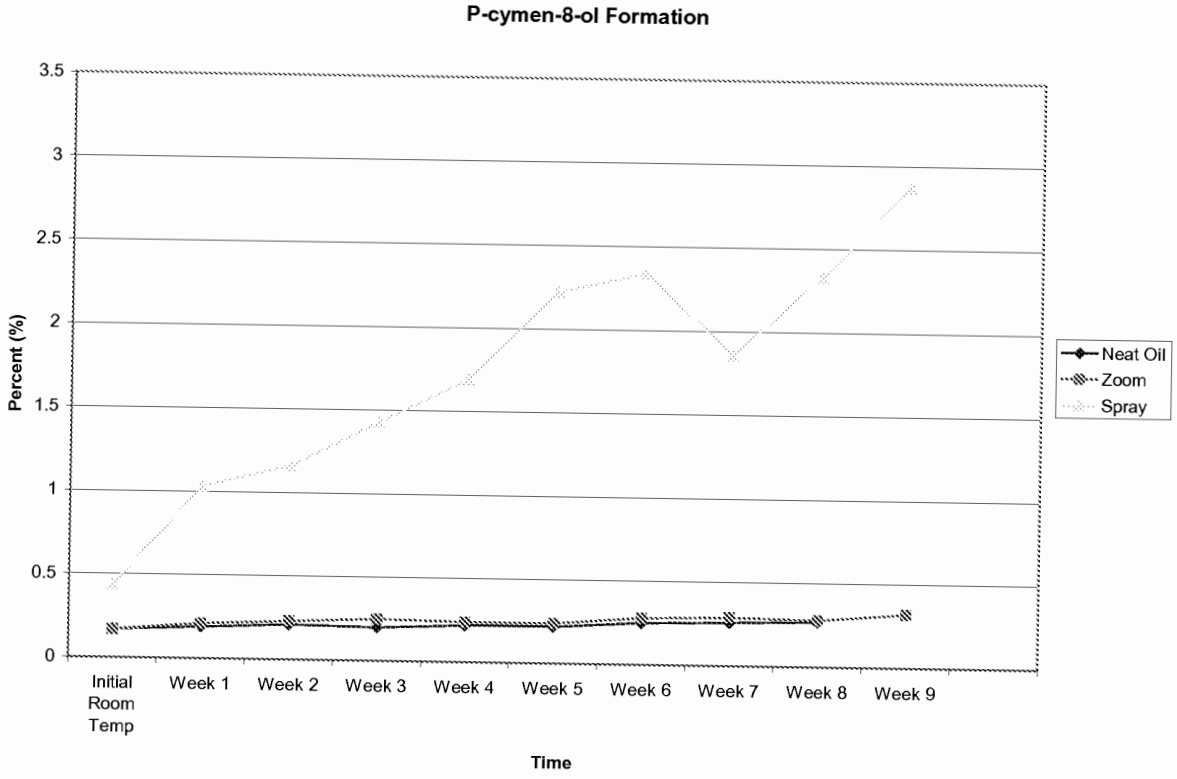

Trans-Carveol & Cis-Carveol Formation
Percent (%)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

FIG. 19


P-cymen-8-ol Formation
Percent (%)
3.5
3
2.5
2
1.5
1
0.5
0
Initial Room Temp
Week 1
Week 2
Week 3
Week 4
Week 5
Week 6
Week 7
Week 8
Week 9
Time
Neat Oil
Zoom
Spray

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. BEETZ
Filer:	Steven John Hultquist
Attorney Docket Number:	4585-101 CIP

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility filing Fee (Electronic filing)	4011	1	70	70
Utility Search Fee	2111	1	300	300
Utility Examination Fee	2311	1	360	360
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**730**

Electronic Acknowledgement Receipt

EFS ID:	21324033
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. BEETZ
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	27-JAN-2015
Filing Date:	
Time Stamp:	17:25:22
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$730
RAM confirmation Number	6704
Deposit Account	083284
Authorized User	HULTQUIST, STEVEN J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	101CIP_ApplicationTransmittal.pdf	37995 b146126a3498c6b42f4212719b43a1ac521fa693	no	1
Warnings:					
Information:					
2	Application Data Sheet	101CIP_ApplicationDataSheet.pdf	102305 bf6f8668ee2f14d438707a00dd55f67f367fa782	no	7
Warnings:					
Information:					
This is not an USPTO supplied ADS fillable form					
3	Oath or Declaration filed	101_DeclarationAsFiled.pdf	993354 b51bfca27235213fb025212c4b6dc9aa09c54d7d	no	4
Warnings:					
Information:					
4	Nonpublication request from applicant.	101CIP_NonPublicationRequest.pdf	22260 3b79231314e83f51e770b24ea2d890fc755d24ba	no	1
Warnings:					
Information:					
5		101CIPPatentApplication.pdf	1603816 235eb3d0a6de5473dc7d10021802a17f0adf2b03	yes	45

Multipart Description/PDF files in .zip description

Document Description	Start	End
Specification	1	23
Claims	24	27
Abstract	28	28
Drawings-other than black and white line drawings	29	45

Warnings:

Information:

6	Fee Worksheet (SB06)	fee-info.pdf	35439 a2b98f8ba389e9a7101b38b9e1a60235391 6b5f1	no	2

Warnings:	
Information:	
Total Files Size (in bytes):	2795169

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

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Electronic Acknowledgement Receipt

EFS ID:	21324033
Application Number:	14606771
International Application Number:	
Confirmation Number:	9733
Title of Invention:	METHODS AND APPARATUS FOR LOW HEAT SPRAY DRYING
First Named Inventor/Applicant Name:	Charles P. BEETZ
Customer Number:	23448
Filer:	Steven John Hultquist
Filer Authorized By:	
Attorney Docket Number:	4585-101 CIP
Receipt Date:	27-JAN-2015
Filing Date:	
Time Stamp:	17:25:22
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$730
RAM confirmation Number	6704
Deposit Account	083284
Authorized User	HULTQUIST, STEVEN J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	101CIP_ApplicationTransmittal.pdf	37995 b146126a3498c6b42f4212719b43a1ac521fa693	no	1
Warnings:					
Information:					
2	Application Data Sheet	101CIP_ApplicationDataSheet.pdf	102305 bf6f8668ee2f14d438707a00dd55f67f367fa782	no	7
Warnings:					
Information:					
This is not an USPTO supplied ADS fillable form					
3	Oath or Declaration filed	101_DeclarationAsFiled.pdf	993354 b51bfca27235213fb025212c4b6dc9aa09c54d7d	no	4
Warnings:					
Information:					
4	Nonpublication request from applicant.	101CIP_NonPublicationRequest.pdf	22260 3b79231314e83f51e770b24ea2d890fc755d24ba	no	1
Warnings:					
Information:					
5		101CIPPatentApplication.pdf	1603816 235eb3d0a6de5473dc7d10021802a17f0adf2b03	yes	45

Multipart Description/PDF files in .zip description

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Specification	1	23
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6	Fee Worksheet (SB06)	fee-info.pdf	35439 a2b98f8ba389e9a7101b38b9e1a60235391 6b5f1	no	2

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