evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in Claims 75, 79, and 84.

For at least the foregoing reasons, Claims 75, 79, and 84, as currently presented, are patentable over **Doane**. Accordingly, the rejection of these Claims under 35 U.S.C. § 103(a) over this reference should be withdrawn.

## F. Conclusion

Claims 74-88, as amended or as currently presented, are patentable over the art relied upon in the present Office Action. Accordingly, Claims 74-88 are in condition for allowance, and favorable action is earnestly solicited thereon.

Should the Examiner feel that there are any issues outstanding after consideration of this response, the Examiner is invited to contact Mr. Matt M. Eslami at 513-248-6193 to expedite prosecution of the above application.

---

Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id*. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

No extension of time is believed to be required. However, the Commissioner is hereby authorized by this paper to charge any fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment, to Deposit Account No. 09-0525. **This paragraph is intended to be a CONSTRUCTIVE PETITION FOR EXTENSION OF TIME in accordance with 37 C.F.R. § 1.136(a)(3) if needed.**

Respectfully Submitted,

Date: December 10, 2010

By: /Matthew M. Eslami/

Matthew M. Eslami
Reg. No. 45,488
Patent Agent for Applicant
International Paper Company
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Tel: (513) 248-6193
Fax: (513) 248-6455
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| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 9007230 |
| **Application Number:** | 11348150 |
| **International Application Number:** | |
| **Confirmation Number:** | 5681 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Customer Number:** | 01726 |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Filer Authorized By:** | Matthew M. Eslami |
| **Attorney Docket Number:** | FDS-029388-US |
| **Receipt Date:** | 10-DEC-2010 |
| **Filing Date:** | 06-FEB-2006 |
| **Time Stamp:** | 10:25:32 |
| **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 | | 101210_rsptooa_fds029388us.pdf | 151952<br>cf0c87394881849850ed3c54f4a3d79a9b7ab0c8 | yes | 12 |

| | Multipart Description/PDF files in .zip description | | |
|---|---|---|---|
| | **Document Description** | **Start** | **End** |
| | Amendment/Req. Reconsideration-After Non-Final Reject | 1 | 1 |
| | Claims | 2 | 4 |
| | Applicant Arguments/Remarks Made in an Amendment | 5 | 12 |
| **Warnings:** | | | |
| **Information:** | | | |
| | **Total Files Size (in bytes):** | 151952 | |

**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.**

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
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 displays a valid OMB control number.

# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | ☐ To be Mailed |
|---|---|---|
| 11/348,150 | 02/06/2006 | |

## 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 | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | 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 $250 ($125 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 | | | TOTAL | |

## APPLICATION AS AMENDED – PART II

| AMENDMENT | 12/10/2010 | (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)) | * 15 | Minus | ** 73 | = 0 | X $ = | | OR | X $52= | 0 |
| | Independent (37 CFR 1.16(h)) | * 2 | Minus | ***13 | = 0 | X $ = | | OR | X $220= | 0 |
| | ☐ 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 | 0 |

| AMENDMENT | | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 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 number found in the appropriate box in column 1.

Legal Instrument Examiner:
/JOY DOBBS/

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.*

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 12/15/2010

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
LOVELAND, OH 45140

| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 12/15/2010 | PAPER |

**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.

| Interview Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 11/348,150 | CLEVELAND ET AL. | |
| | Examiner | Art Unit | |
| | MARC A. PATTERSON | 1782 | |

All participants (applicant, applicant's representative, PTO personnel):

(1) *Marc Patterson*. (3)_____.

(2) *Eric Guttag*. (4)_____.

Date of Interview: *07 December 2010*.

Type: a)☒ Telephonic b)☐ Video Conference
c)☐ Personal [copy given to: 1)☐ applicant 2)☐ applicant's representative]

Exhibit shown or demonstration conducted: d)☐ Yes e)☒ No.
If Yes, brief description: _____.

Claim(s) discussed: *all of the record*.

Identification of prior art discussed: *all of the record*.

Agreement with respect to the claims f)☐ was reached. g)☒ was not reached. h)☐ N/A.

Substance of Interview including description of the general nature of what was agreed to if an agreement was reached, or any other comments: *The claimed invention vs the prior art of record, specifically if the claimed invention is disclosed by the prior art of record.* .

(A fuller description, if necessary, and a copy of the amendments which the examiner agreed would render the claims allowable, if available, must be attached. Also, where no copy of the amendments that would render the claims allowable is available, a summary thereof must be attached.)

THE FORMAL WRITTEN REPLY TO THE LAST OFFICE ACTION MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a reply to the last Office action has already been filed, APPLICANT IS GIVEN A NON-EXTENDABLE PERIOD OF THE LONGER OF ONE MONTH OR THIRTY DAYS FROM THIS INTERVIEW DATE, OR THE MAILING DATE OF THIS INTERVIEW SUMMARY FORM, WHICHEVER IS LATER, TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW. See Summary of Record of Interview requirements on reverse side or on attached sheet.

| /Marc A Patterson/<br>Primary Examiner, Art Unit 1782 | |
|---|---|



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
Page 407 of 1179

# Summary of Record of Interview Requirements

**Manual of Patent Examining Procedure (MPEP), Section 713.04, Substance of Interview Must be Made of Record**
A complete written statement as to the substance of any face-to-face, video conference, or telephone interview with regard to an application must be made of record in the application whether or not an agreement with the examiner was reached at the interview.

**Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews**
Paragraph (b)

In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the applicant. An interview does not remove the necessity for reply to Office action as specified in §§ 1.111, 1.135. (35 U.S.C. 132)

37 CFR §1.2 Business to be transacted in writing.
All business with the Patent or Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

———

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete an Interview Summary Form for each interview held where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below. Where the substance of an interview is completely recorded in an Examiners Amendment, no separate Interview Summary Record is required.

The Interview Summary Form shall be given an appropriate Paper No., placed in the right hand portion of the file, and listed on the "Contents" section of the file wrapper. In a personal interview, a duplicate of the Form is given to the applicant (or attorney or agent) at the conclusion of the interview. In the case of a telephone or video-conference interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the interview rather than with the next official communication.

The Form provides for recordation of the following information:
- Application Number (Series Code and Serial Number)
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (telephonic, video-conference, or personal)
- Name of participant(s) (applicant, attorney or agent, examiner, other PTO personnel, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). Note: Agreement as to allowability is tentative and does not restrict further action by the examiner to the contrary.
- The signature of the examiner who conducted the interview (if Form is not an attachment to a signed Office action)

It is desirable that the examiner orally remind the applicant of his or her obligation to record the substance of the interview of each case. It should be noted, however, that the Interview Summary Form will not normally be considered a complete and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview.

A complete and proper recordation of the substance of any interview should include at least the following applicable items:
1) A brief description of the nature of any exhibit shown or any demonstration conducted,
2) an identification of the claims discussed,
3) an identification of the specific prior art discussed,
4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the Examiner,
5) a brief identification of the general thrust of the principal arguments presented to the examiner,
   (The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments is not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application file. Of course, the applicant may desire to emphasize and fully describe those arguments which he or she feels were or might be persuasive to the examiner.)
6) a general indication of any other pertinent matters discussed, and
7) if appropriate, the general results or outcome of the interview unless already described in the Interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete and accurate, the examiner will give the applicant an extendable one month time period to correct the record.

**Examiner to Check for Accuracy**

If the claims are allowable for other reasons of record, the examiner should send a letter setting forth the examiner's version of the statement attributed to him or her. If the record is complete and accurate, the examiner should place the indication, "Interview Record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.

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UNITED STATES DEPARTMENT OF COMMERCE
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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 02/02/2011

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
LOVELAND, OH 45140

| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 02/02/2011 | PAPER |

**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.

| Office Action Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 11/348,150 | CLEVELAND ET AL. | |
| | Examiner | Art Unit | |
| | MARC A. PATTERSON | 1782 | |

*-- 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 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, 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 *10 December 2010*.

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

3)☐ 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**

4)☒ Claim(s) *74-88* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *74-88* is/are rejected.

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

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

**Application Papers**

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

10)☐ 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).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**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).

a)☐ All b)☐ Some * c)☐ None of:

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) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

## DETAILED ACTION

WITHDRAWN REJECTIONS

1. The 35 U.S.C. 102(b) rejection of Claims 74, 81 - 83 and 85 - 88 as being anticipated by Doane et al (U.S. Patent No. 6,040,063), of record on page 2 of the previous Action, withdrawn.

2. The 35 U.S.C. 103(a) rejection of Claims 75 and 84 as being unpatentable over Doane et al (U.S. Patent No. 6,040,063), of record on page 2 of the previous Action, withdrawn.

NEW REJECTIONS

**Claim Rejections – 35 USC § 102(b)**

3. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

4. Claims 74, 81 - 83 and 85 - 88 are rejected under 35 U.S.C. 102(b) as being anticipated by Asrar et al. (U.S. Patent No. 6,025,028).

With regard to Claim 74, Asrar et al discloses a laminate comprising a substrate (paper bag; column 10, line 59 – 61) having a heat – sealable coating (column 10, lines 59 – 61), therefore an interior layer, which is a moisture protective layer comprising biodegradable polyester (column 1, line 7 – 11)

With regard to Claims 81 - 83 and 87 - 88, Asrar et al discloses polyester comprising polyhydroxyalkanoate (column 10, line 54 – 55) and a filler comprising calcium carbonate (column 8, lines 59 – 60).

With regard to Claims 85 - 86, the laminate is a cup (tray; column 10, lines 59 – 61).

5. Claims 76 – 78 and 80 are rejected under 35 U.S.C. 102(b) as being anticipated by Doane et al. (U.S. Patent No. 6,040,063).

With regard to Claim 76, Doane et al discloses a laminate comprising substrate comprising a substrate (column 4, lines 32 - 39) and an interior and exterior moisture protective layer (coating '16' in Figure 2; column 4, lines 29 - 31) comprising biodegradable polyester (column 4, line 52).

With regard to Claims 77 – 78 and 80, Doane et al discloses polyester comprising polyhydroxyalkanoate (column 10, line 42) and a filler comprising calcium carbonate (column 9, line 41).

**Claim Rejections – 35 USC § 103(a)**

6. The following is a quotation of 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.

7. Claims 75 and 84 are rejected under 35 U.S.C. 103(a) as being unpatentable over Asrar et al. (U.S. Patent No. 6,025,028).

Asrar et al disclose a laminate as discussed above. With regard to Claims 75 and 84, Asrar et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Asrar et al discloses layers comprised in a cup, as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

8. Claim 79 is rejected under 35 U.S.C. 103(a) as being unpatentable over Doane et al. (U.S. Patent No. 6,040,063).

Doane et al disclose a laminate as discussed above. Doane et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Doane et al discloses layers comprised in a tray (column 4, lines 10 - 13), as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

ANSWERS TO APPLICANT'S ARGUMENTS

9. Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 74, 76 - 78, 80 - 83 and 85 – 88 as being anticipated by Doane et al. (U.S. Patent No. 6,040,063) and 35 U.S.C. 103(a) rejection of Claims 75, 79 and 84 as being unpatentable over Doane et al. (U.S. Patent No. 6,040,063), of record in the previous Action, have been considered and have been found to be persuasive. The rejections are therefore withdrawn. The new rejections above are directed to amended Claims 74 - 88.

10. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

11. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497. The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Rena Dye can be reached on 571-272-1498. 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).

/Marc A Patterson/
Primary Examiner, Art Unit 1782

| Notice of References Cited | Application/Control No. 11/348,150 | Applicant(s)/Patent Under Reexamination CLEVELAND ET AL. | |
|---|---|---|---|
| | Examiner MARC A. PATTERSON | Art Unit 1782 | Page 1 of 1 |

**U.S. PATENT DOCUMENTS**

| * | | Document Number Country Code-Number-Kind Code | Date MM-YYYY | Name | Classification |
|---|---|---|---|---|---|
| * | A | US-6,025,028 | 02-2000 | Asrar et al. | 427/358 |
| | B | US- | | | |
| | 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 | 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.



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
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PTO/SB/30EFS (07-09)
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.

# REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
## (Submitted Only via EFS-Web)

| Application Number | 11/348,150 | Filing Date | 2006-02-06 | Docket Number (if applicable) | FDS-029388-US | Art Unit | 1782 |
|---|---|---|---|---|---|---|---|
| First Named Inventor | Christopher S. Cleveland | | | Examiner Name | Patterson, Marc A. | | |

**This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.**
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

☐ Other _____

☒ Enclosed

☒ Amendment/Reply

☐ Information Disclosure Statement (IDS)

☐ Affidavit(s)/ Declaration(s)

☐ Other _____

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____
(Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

☒ **The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**
The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 090525

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

☐ Applicant Signature

PTO/SB/30EFS (07-09)
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.

| Signature of Registered U.S. Patent Practitioner | | | |
|---|---|---|---|
| Signature | /Matthew M. Eslami/ | Date (YYYY-MM-DD) | 2011-03-29 |
| Name | Matthew M. Eslami | Registration Number | 45488 |

This collection of information is required by 37 CFR 1.114. 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.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

## 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 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.



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
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| Electronic Patent Application Fee Transmittal | |
|---|---|
| **Application Number:** | 11348150 |
| **Filing Date:** | 06-Feb-2006 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Attorney Docket Number:** | FDS-029388-US |
| Filed as Large Entity | |

**Utility under 35 USC 111(a) Filing Fees**

| 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:** | | | | |
| **Extension-of-Time:** | | | | |

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Miscellaneous:** | | | | |
| Request for continued examination | 1801 | 1 | 810 | 810 |
| | | **Total in USD ($)** | | **810** |

| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 9768651 |
| **Application Number:** | 11348150 |
| **International Application Number:** | |
| **Confirmation Number:** | 5681 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Customer Number:** | 01726 |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Filer Authorized By:** | Matthew M. Eslami |
| **Attorney Docket Number:** | FDS-029388-US |
| **Receipt Date:** | 30-MAR-2011 |
| **Filing Date:** | 06-FEB-2006 |
| **Time Stamp:** | 08:20:59 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| | |
|---|---|
| Submitted with Payment | yes |
| Payment Type | Deposit Account |
| Payment was successfully received in RAM | $810 |
| RAM confirmation Number | 7631 |
| Deposit Account | 090525 |
| Authorized User | |
| The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:<br>Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees)<br>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 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance 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 | | 110329_rsptofnloa_fds029388us.pdf | 192457<br>64344b069077b2b1d1f7be1c93df9e2184a86445 | yes | 16 |

| | Multipart Description/PDF files in .zip description | | |
|---|---|---|---|
| | **Document Description** | **Start** | **End** |
| | Amendment After Final | 1 | 1 |
| | Claims | 2 | 4 |
| | Applicant Arguments/Remarks Made in an Amendment | 5 | 16 |

| | | | | | |
|---|---|---|---|---|---|
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 2 | Request for Continued Examination (RCE) | 110329_rce_fds029388us.pdf | 38862<br>d55cab8074b01e5c306653d4b6c90f0956d9eb9f | no | 3 |
| **Warnings:** | | | | | |
| This is not a USPTO supplied RCE SB30 form. | | | | | |
| **Information:** | | | | | |
| 3 | Fee Worksheet (PTO-875) | fee-info.pdf | 30390<br>fe683d5676324c071eef91923e1d1f8827717c0a | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 261709 | | |

**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.**

Docket No.: FDS-029388-US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

| | | |
|---|---|---|
| CLEVELAND, et al. | : | GROUP ART UNIT: 1782 |
| SERIAL NO: 11/348,150 | : | EXAMINER: PATTERSON, MARC A. |
| FILED: February 06, 2006 | : | CONFIRMATION #: 5681 |

FOR: BIODEGRADABLE PAPER-BASED LAMINATE WITH OXYGEN AND MOISTURE BARRIER PROPERTIES AND METHOD FOR MAKING BIODEGRADABLE PAPER-BASED LAMINATE

**AMENDMENT AFTER FINAL REJECTION PURSUANT TO 37 CFR 1.116(b)**

United States Patent and Trademark Office
**Customer Service Window, Mail Stop AAF**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In response to the Office Action (made FINAL) mailed February 2, 2011, the period for response which is set to expire May 2, 2011, please amend the above-captioned application follows, as well as consider the following remarks. Applicants submit there are good and sufficient reasons, in accordance with 37 CFR 1.116(b), for entering these amendments. In particular, in view of the following remarks, it is believed these amendments will put the above application in better condition for allowance or appeal.

Applicants respectfully request prompt issuance of a Notice of Allowance or an Advisory Action by the Examiner, as the present amendment is being timely filed on or before two months of the mailing date of the Final Office Action (*i.e.*, on or before April 2, 2011). See MPEP § 706.07(f). Applicants' representative, Matthew M Eslami, also respectfully requests a telephone conference in the event the Examiner has any questions, comments or suggestions that would place any pending claim not in allowable form in better condition for allowance. Applicant's representative may be reached directly at 513-248-6193 .

**Amendments to/Listing of the Claims** begin on page **2** of this paper.

**Remarks/Arguments** begin on page **5** of this paper.

**IN THE CLAIMS**

The listing of claims will replace all prior versions, and listings, of claims in the application:

**Listing of Claims:**

Claims 1-73. (Canceled).

74. (Currently Amended) A product in the form of a cup comprising a laminate [for] forming a moisture barrier, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface; and

a moisture protectant layer disposed solely on said interior surface of said substrate and comprising at least one biodegradable polyester polymer.

75. (Currently Amended) The product [laminate] according to claim 74, wherein the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

76. (Currently Amended) A product in the form of a cup comprising a laminate [for] forming moisture barriers, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface;

a first moisture barrier layer disposed on said interior surface of said substrate; and

a second moisture protectant layer disposed on said exterior surface of said substrate and comprising at least one biodegradable polyester polymer, wherein the second moisture barrier layer is separate from the first moisture barrier layer disposed on said interior surface of said substrate.

77. (Currently Amended) The product [laminate] according to Claim 88, wherein the second moisture protectant layer further comprises at least one filler.

78. (Currently Amended) The product [laminate] according to Claim 77, wherein the second

moisture protectant layer comprises at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

79. (Currently Amended) The product [laminate] according to claim 76, wherein the second moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

80. (Currently Amended) The product [laminate] according to Claim 76, wherein the second moisture protectant layer further comprises at least one filler selected from the group consisting of calcium carbonate and starch.

81. (Currently Amended) The product [laminate] according to Claim 87, wherein the moisture protectant layer further comprises at least one filler.

82. (Currently Amended) The product [laminate] according to 81, wherein the moisture protectant layer comprises at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

83. (Currently Amended) The product [laminate] according to Claim 74, wherein the moisture protectant layer further comprises at least one member selected from the group consisting of calcium carbonate and starch.

84. (Currently Amended) The product [laminate] according to Claim 74, wherein the substrate comprises paperboard; and the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$ and comprises polylactic acid and at least one member selected from the group consisting of calcium carbonate and starch.

85-86 (Cancelled).

87. (Currently Amended) The product [laminate] according to claim 74, wherein the at least one biodegradable polyester polymer is selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

88. (Currently Amended) The product [laminate] according to claim 76, wherein the second moisture protectant layer comprises at least one biodegradable polyester polymer selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

**REMARKS/ARGUMENTS**

**A. Status of Claims**

Favorable reconsideration of this application is respectfully requested. Claims 1-73 have previously been cancelled. Claims 85-86 are currently cancelled. Claims 74-84 and 87-88 are currently pending.

**B. Procedural Matters**

Applicants gratefully acknowledge the Examiner's statements at pages 2 and 5 of the Final Office Action (hereafter "Final Action") that the prior rejection of Claims 74, 81-83 and 85-88 under 35 U.S.C. § 102(b) as being anticipated by U.S. Pat. No. 6,040,063 to Doane et al (hereafter referred to as "**Doane**") has been withdrawn in view of the persuasiveness of Applicants' arguments in their prior amendment of December 10, 2010.

Applicants also gratefully acknowledge the Examiner's statements at pages 2 and 5 of the Final Action that the prior rejection of Claims 75 and 84 under 35 U.S.C. § 103(a) as being unpatentable over **Doane** has been withdrawn in view of the persuasiveness of Applicants' arguments in their prior amendment of December 10, 2010.

**C. Amendments to Claims**

Claim 74 and Claim 85 (now cancelled) have been combined and amended to recite a **product in the form of a cup comprising** a laminate forming a moisture barrier, **said laminate** comprising a substrate having a separate interior product contacting surface and a separate exterior surface, wherein the moisture protectant layer is disposed solely on the interior surface of the substrate. Support for the amendments to Claim 74 may also be found, for example, in paragraphs [0014] and [0048] of the present application.

In view of the amendments to Claim 74, the language of dependent Claims 75, 81-84, and 87 has been amended accordingly.

Claim 76 has been similarly amended to recite a **product in the form of a cup comprising** a laminate forming moisture barriers, **said laminate** comprising: a substrate having a separate interior product contacting surface and a separate exterior surface; a first moisture barrier layer disposed on said interior surface of said substrate; and a second moisture protectant layer disposed on said exterior surface of said substrate and comprising at

least one biodegradable polyester polymer, wherein the second moisture barrier layer is separate from the first moisture barrier layer disposed on said interior surface of said substrate. Support for the amendments to Claim 76 may also be found, for example, in paragraphs [0014] and [0048] of the present application.

In view of the amendments to Claim 76, the language of dependent Claims 77-80 and 88 has been amended accordingly.

**D. Response to Rejection of Claims 74, 81-83, and 85-88 under 35 U.S.C. § 102(b) as Being Anticipated by Asrar**

At pages 2-3 of the Final Action, Claims 74, 81-83, and 85-88 have been rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Pat. No. 6,025,028 to Asrar et al (hereafter referred to as "**Asrar**"). **This rejection is respectfully traversed with respect to Claims 74, 81-83, and 87-88**,[1] as amended, for at least the following reasons.

In support of the rejection of Claims 74 and 85-86 as being anticipated by **Asrar**, the Final Action makes the following allegations:

> ***Allegation 1***: [**Asrar**] discloses a laminate comprising a substrate (paper bag; column 10, lines 59-61) having a heat-sealable coating, **therefore an interior layer**, which is a moisture protective layer comprising [a] biodegradable polyester (column 1, lines 7-11).[2]
>
> ***Allegation 2***: **[T]he laminate is a cup** (**tray**; column 10, lines 59-61).[3]

In response to what Allegations 1 and 2 assert, Claim 74 and Claim 85 (now cancelled) have been combined and amended to recite a **product in the form of a cup comprising** the laminate forming a moisture barrier, **said laminate** comprising a substrate having a separate interior product contacting surface and a separate exterior surface, wherein the moisture protectant layer is disposed solely on the interior surface of the substrate. As amended, Claim 74 is distinguishable over the teachings of **Asrar** at least with respect to the following features: (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**; (2) wherein the moisture protectant layer is disposed

[1] Claims 85 and 86 have been cancelled, so this rejection with respect to those Claims is now moot and will be addressed with respect to Claim 74, as amended to incorporate the language of Claim 85.
[2] See pages 2 of the Final Action (emphasis added).
[3] See page 3 of the Final Action (emphasis added).

**solely** on the interior surface of the substrate. Contrary to what Allegation 1 asserts, **Asrar** does not teach that its coating (a) is on the interior surface of the substrate when in the form of a cup, and especially (b) is solely on the interior surface of the substrate. Instead, all that **Asrar** says in column 10, lines 59-61, relied upon by Allegations 1 and 2 is that the "[p]referred objects suitable for coating" include "cups, paper, paper waste bags, etc." Nothing described in column 10, lines 59-61, of **Asrar** relied upon by Allegations 1 and 2 (or in any other portion of **Asrar**) can be construed as teaching features (1) or (2) of the cup recited in amended Claim 74.

If the Examiner still maintains that **Asrar** teaches (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**, (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate according to amended Claim 74 based on what is asserted in Allegations 1 and 2, then Applicants assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claim 74 under 35 U.S.C. § 102(b) as being anticipated by **Asrar** for the reasons presented in Allegations 1 and 2, Applicants **respectfully request** that he provides an affidavit/declaration under 37 CFR § 1.104(d)(2)[4] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 81-83, and 87-88 as being anticipated by **Asrar**, the Final Action makes the following allegation:

---

[4] See 37 CFR § 1.104(d)(2) which states: "When a rejection in an application is based on facts within the personal knowledge of an employee of the Office, the data shall be as specific as possible, and the reference must be supported, when called for by the applicant, by the affidavit of such employee, and such affidavit shall be subject to contradiction or explanation by the affidavits of the applicant and other persons." Applicants note that in the unpublished case of *In re Sun*, 31 USPQ2d 1451, 1455 (Fed. Cir. 1993), the USPTO argued "the procedures established by 37 C.F.R. Section 1.107(b) (1993) [now 37 CFR § 1.104(d)(2)] ***expressly entitle*** an Applicant, on mere request, to an examiner affidavit that provides [citations that support the Examiner's asserted level of skill in the art]" (emphasis added). Furthermore, in *In re Sun*, the Federal Circuit, held that "this procedure, so readily available, helps save the lack of citation in an office action from possible constitutional infirmity in denying reasonable notice and hence due process." See 31 USPQ2d at 1455. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 18): "If it is not possible for the examiner to provide this type of information, **the examiner might choose instead to provide an affidavit detailing the examiner's own personal knowledge** (as a person approximating one of ordinary skill in the art) of the technology in question (citing 37 CFR § 1.104(d)(2)) (emphasis added)."

> ***Allegation 3***: [**Asrar**] discloses [a] polyester comprising polyhydroxyalkanoate (column 10, line[s] 54-55) and a **filler** comprising calcium carbonate (column 8, lines 59-60).[5]

What Allegation 3 asserts also does not support the rejection of amended Claims 81-83 and 87-88 as being anticipated by **Asrar**. Amended Claims 81-83 and 87 depend, directly or indirectly, from amended Claim 74. Accordingly, amended Claims 81-83 and 87 are patentable over **Asrar** for at least the same reasons presented above in response to Allegations 1 and 2 for why amended Claim 74 is patentable over this reference.

In addition, amended Claims 81-83 are further distinguishable over **Asrar** in reciting that the moisture protectant layer comprises **at least one filler** which may be calcium carbonate (see amended Claim 82). First, Allegation 3 has **mischaracterized** what is fairly taught by **Asrar** with regard to the use of calcium carbonate. Contrary to what Allegation 3 asserts, **Asrar** does not teach that calcium carbonate is being used as a filler according to amended Claims 81-83. Instead, **Asrar** teaches inorganic compounds such as metal oxides, metal hydroxides, and metal carbonates, preferably of metals such as aluminum, antimony, tin, sodium, calcium, magnesium, barium or zinc, "can be used to further improve nucleation activity and/or reduce the extent of discoloration and/or improve the clarity of PHA-derived products when used in combination" with ODPA nucleants to form **Asrar's** coating comprising the PHAs.[6] Nothing in **Asrar** suggests that calcium carbonate is being used as a filler according to amended Claims 81-83.

If the Examiner still maintains that **Asrar** teaches **at least one filler** in the moisture protectant layer according to amended Claims 81-83 based on what is asserted in Allegation 3, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 81-83 under 35 U.S.C. § 102(b) as being anticipated by **Asrar** for the reasons presented in Allegation 3, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been

[5] See page 3 of the Final Action (emphasis added).
[6] See column 8, lines 53-63, of **Asrar**.

provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

Amended Claim 88 depends from amended Claim 76. But the Final Action has not rejected amended Claim 76 as anticipated or otherwise unpatentable over **Asrar**. Accordingly, like amended Claim 76, amended Claim 88 must also be patentable over **Asrar**.

For at least the foregoing reasons, Claims 74, 81-83, and 87-88, as amended, are patentable over **Asrar**. Accordingly, the rejection of these Claims under 35 U.S.C. § 102(b) based this reference should be withdrawn.

**E. Response to Rejection of Claims 76-78 and 80 under 35 U.S.C. § 102(b) as Being Anticipated by Doane**

At page 3 of the Final Action, Claims 76-78 and 80 have been rejected under 35 U.S.C. § 102(b) as being anticipated by **Doane**. **This rejection is respectfully traversed with respect to these Claims**, as amended, for at least the following reasons.

In support of the rejection of Claim 76 as being anticipated by **Doane**, the Final Action makes the following allegation:

> ***Allegation 4***: [**Doane**] discloses a laminate comprising [a] substrate (column 4, lines 32-39) and **an interior and exterior moisture protective layer** (coating '16' in Figure 2; column 4, lines 29-31) comprising [a] biodegradable polyester (column 4, line 52).[7]

In response to what Allegation 4 asserts, Claim 76 has been amended to recite a **product in the form of a cup comprising** a laminate forming moisture barriers, **said laminate** comprising: a substrate having a separate interior product contacting surface and a separate exterior surface; a first moisture barrier layer disposed on said interior surface of said substrate; and a second moisture protectant layer disposed on said exterior surface of said substrate and comprising at least one biodegradable polyester polymer, wherein the second moisture barrier layer is separate from the first moisture barrier layer disposed on said interior surface of said substrate.

Amended Claim 76 is distinguishable over **Doane** in reciting that the second moisture barrier layer of the laminate of the cup, which is disposed on the exterior substrate surface, **is**

[7] See page 3 of the Final Action (emphasis added).

**separate from the first moisture barrier layer disposed on the interior substrate surface**. In other words, amended Claim 76 recites **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate**. By contrast, and contrary to what Allegation 4 asserts, coating layer 16 of **Doane** forms only **one continuous and surrounding exterior layer** with respect structure 12. In fact, and contrary to the requirements of 37 CFR § 1.104(c)(2)[8] and MPEP § 707.05,[9] Allegation 4 provides a **completely inadequate explanation** as to how **Doane** teaches **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to amended Claim 76.

If the Examiner still maintains that **Doane** teaches a **cup** comprising a laminate having **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to amended Claim 76 based on what is asserted in Allegation 4, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claim 76 under 35 U.S.C. § 102(b) as being anticipated by **Doane** for the reasons presented in Allegation 3, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 77-78 and 80 as being anticipated by **Doane**, the Final Action makes the following allegation:

> ***Allegation 5***: [**Doane**] discloses [a] polyester comprising polyhydroxyalkanoate (column 10, line 42) and a **filler** comprising calcium carbonate (column 9, line 41).[10]

What Allegation 5 asserts also does not support the rejection of amended Claims 77-78 and

[8] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)
[9] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)
[10] See page 3 of the present Office Action (emphasis added).

80 as being anticipated by **Doane**. Amended Claims 77-78 and 80 depend, directly or indirectly, from amended Claim 76. Accordingly, amended Claims 77-78 and 80 are patentable over **Doane** for at least the same reasons presented above in response to Allegation 4, for why amended Claim 76 is patentable over this reference.

In addition, amended Claims 77-78 and 80 are further distinguishable over **Doane** in reciting that the moisture protectant layer comprises **at least one filler** which may be calcium carbonate (see amended Claims 78 and 80). First, Allegation 5 has **mischaracterized** what is fairly taught by **Doane** with regard to the use of calcium carbonate. Contrary to what Allegation 5 asserts, **Doane** does not teach that calcium carbonate is being used as a filler according to Claims 77-78 and 80. Instead, **Doane** teaches that calcium carbonate is being used as a "nucleating agent" for a foamable composition.[11]

Second, these "nucleating agents" are taught by **Doane** for use **in preparing natural polymer foams for structure 12**,[12] and not hydroxyfunctional polyester layer 14 which is self-adhered **to the exterior surface** of structure 12. In other words, and contrary to what Allegation 5 asserts, **Doane** does not teach inclusion of calcium carbonate (or any other disclosed "nucleating agent") in its hydroxyfunctional polyester layer 14 (or layer 16), much less the moisture protectant layers of amended Claims 77-78 and 80. In fact, the Examiner previously agreed at an November 29, 2010 Interview[13] that **Doane** does not teach inclusion of calcium carbonate or any other "filler" in the moisture protectant layers of amended Claims 77-78 and 80.

If the Examiner still maintains that **Doane** teaches **at least one filler** in the moisture protectant layer according to amended Claims 77-78 and 80 based on what is asserted in Allegation 5, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 77-78 and 80 under 35 U.S.C. § 102(b) as being anticipated by **Doane** for the reasons presented in Allegation 2, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have

[11] See column 9, lines 33-41, of **Doane**.
[12] See, for example, column 7, lines 53-56, and column 9, lines 4-6, of **Doane**.
[13] See page 9 of Applicants' prior amendment of December 10, 2010.

not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claims 76-78 and 80, as amended, are patentable over **Doane**. Accordingly, the rejection of these Claims under 35 U.S.C. § 102(b) based on this reference should be withdrawn.

**F. Response to Rejection of Claims 75 and 84 under 35 U.S.C. § 103(a) as Being Unpatentable over Asrar**

At page 4 of the Final Action, Claims 75 and 84 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**. **This rejection is respectfully traversed with respect to these Claims**, as amended, for at least the following reasons.

In support of the rejection of Claims 75 and 84 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, the Final Action makes the following allegation:

> ***Allegation 6***: [**Asrar**] discloses a laminate as discussed above. With regard to Claims 75 and 84, [**Asrar**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Asrar**] discloses layers comprised in a cup, as discussed above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[14]

What Allegation 6 asserts does not support the rejection of amended Claims 75 or 84 as being unpatentable over **Asrar**, for at least the following reasons. First, for at least the reasons presented above in response to Allegations 1 and 2, amended Claim 74 is patentable over **Asrar**. Allegation 6 does not assert that those features of amended Claim 74 (i.e., a cup comprising a laminate having a moisture barrier layer **which is disposed solely on the interior product contacting surface**) which were asserted **to be missing from the teachings** of **Asrar** are now taught by that reference. Amended Claims 75 and 84 also depend directly from amended Claim 74, and are therefore patentable over **Asrar** for at least

[14] See page 4 of the Final Action (emphasis added).

the same reasons presented above in response to Allegations 1 and 2 for why amended Claim 74 is patentable over this reference.

Second, Allegation 6 concedes that the coat weights (not **thickness** as asserted in Allegation 6) recited in amended Claims 75 and 84 are not taught by **Asrar**. Instead, Allegation 6 asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually unsupported** by **Asrar**, the reference relied upon in rejecting amended Claims 75 and 84. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[15]

Allegation 6 points to **absolutely nothing** in **Asrar** (or any other verifiable evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in amended Claims 75 and 84. In fact, it again appears that the Examiner is rejecting amended Claims 75 and 84 as being unpatentable over **Asrar** based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 75 and 84 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar** for the reasons presented in Allegation 6, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

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[15] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc*., 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id*. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

For at least the foregoing reasons, Claims 75 and 84, as amended, are patentable over **Asrar**. Accordingly, the rejection of these Claims under 35 U.S.C. § 103(a) over this reference should be withdrawn.

**G. Response to Rejection of Claim 79 under 35 U.S.C. § 103(a) as Being Unpatentable over Doane**

At page 4 of the Final Action, Claim 79 has been rejected under 35 U.S.C. § 103(a) as being unpatentable over **Doane**. **This rejection is respectfully traversed with respect to this Claim**, as amended, for at least the following reasons.

In support of the rejection of Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane**, the Final Action makes the following allegation:

> ***Allegation 7***: [**Doane**] discloses a laminate as discussed above. [**Doane**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Doane**] discloses layers comprised in a tray (column 4, lines 10-13), as discussed above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[16]

What Allegation 7 asserts does not support the rejection of amended Claim 79 as being unpatentable over **Doane** for at least the following reasons. First, for at least the reasons presented above in response to Allegation 4, amended Claim 76 is patentable over **Doane**. Allegation 6 does not assert that those features in amended Claim 76 (i.e., the second moisture barrier layer disposed on the exterior substrate surface **is separate from the first moisture barrier layer disposed on the interior substrate surface**) which were asserted **to be missing from the teachings** of **Doane** are now taught by that reference. Amended Claim 79 also depends directly from amended Claim 76, and is therefore patentable over **Doane** for at least the same reasons presented above in response to Allegation 4 for why amended Claim 76 is patentable over this reference.

Second, Allegation 7 concedes that the coat weights (not **thickness** as asserted by Allegation 7) recited in amended Claim 79 are not taught by **Doane**. Instead, Allegation 7

[16] See page 4 of the Final Action (emphasis added).

asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion again amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually unsupported** by **Doane**, the reference relied upon in rejecting amended Claim 79. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[17]

Allegation 7 points to **absolutely nothing** in **Doane** (or any other verifiable evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in amended Claim 79. In fact, it again appears that the Examiner is rejecting amended Claim 79 as being unpatentable over **Doane** based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane** for the reasons presented in Allegation 7, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claim 79, as amended, is patentable over **Doane**. Accordingly, the rejection of this Claim under 35 U.S.C. § 103(a) over this reference should be withdrawn.

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[17] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id.* See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

**H. Conclusion**

Claims 74-84 and 87-88, as amended, are patentable over the art relied upon in the Final Action. Accordingly, Claims 74-84 and 87-88 are in condition for allowance, and favorable action is earnestly solicited thereon.

Should the Examiner feel that there are any issues outstanding after consideration of this response, the Examiner is invited to contact Mr. Matthew M. Eslami at 513-248-6193 to expedite prosecution of the above application.

No extension of time is believed to be required. However, the Commissioner is hereby authorized by this paper to charge any fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment, to Deposit Account No. 09-0525. **This paragraph is intended to be a CONSTRUCTIVE PETITION FOR EXTENSION OF TIME in accordance with 37 C.F.R. § 1.136(a)(3) if needed.**

Respectfully Submitted,

Date: March 29, 2011

By: /Matthew M. Eslami/

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**( Not for submission under 37 CFR 1.99)**

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|---|---|
| Application Number | 11348150 |
| Filing Date | 2006-02-06 |
| First Named Inventor | CLEVELAND, CS |
| Art Unit | 1782 |
| Examiner Name | Patterson, Marc A. |
| Attorney Docket Number | FDS-029388-US |

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| | 2 | 1541345 | EP | | 2003-07-10 | Mitsubishi Plastics, Inc. | | ☐ |
| | 3 | 1630195 | EP | | 2005-08-16 | Sony Corporation | | ☐ |

| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
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| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

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|---|---|---|---|---|---|---|---|---|
| | 4 | 2006328138 | JP | | 2006-12-07 | Matsushita Electric Works Ltd | | ☐ |
| | 5 | 200830332 | JP | | 2008-02-14 | Mitsui Chemicals Inc. | | ☐ |
| | 6 | 1644794 | CN | | 2005-07-27 | Changchun Applied Chemistry | | ☐ |
| | 7 | 2394779 | CN | | 2000-09-06 | Chao Zaizhao | | ☐ |
| | 8 | 2004106630 | WO | | 2004-12-09 | | | ☐ |
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| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

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| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
|---|---|---|
| | Application Number | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

**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 | /Matthew M. Eslami/ | Date (YYYY-MM-DD) | 2011-03-30 |
|---|---|---|---|
| Name/Print | Matthew M. Eslami | Registration Number | 45488 |

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.

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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.

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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权利要求书 2 页 说明书 7 页

[54] 发明名称

聚乳酸/天然纤维复合材料及其生产方法

[57] 摘要

本发明公开了一种聚乳酸/天然纤维复合材料，主要由聚乳酸树脂和天然纤维组成。该复合材料的生产方法包括先将天然纤维用偶联剂溶液进行表面处理，再将天然纤维与聚乳酸树脂及抗氧剂、成核剂、润滑剂混合，熔融挤出造粒，得产品。本发明方法具有操作简单、生产效率高等优点，制备的聚乳酸/天然纤维复合材料，具有较高的模量和耐热性，以及较好的成型加工性，同时又保持了聚乳酸的可生物降解性，可广泛应用于汽车、建筑和居家装饰等领域。

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1、一种聚乳酸/天然纤维复合材料，其特征是该复合材料主要由下列重量组份组成：

| | |
|---|---|
| 聚乳酸 | 60～95 份 |
| 天然纤维 | 5～40 份 |
| 抗氧剂 | 0～1 份 |
| 成核剂 | 0～2 份 |
| 润滑剂 | 0～1 份。 |

2、根据权利要求 1 所述的聚乳酸/天然纤维复合材料，其特征是所述的天然纤维包括大麻纤维、棉纤维、竹纤维、苎麻纤维、亚麻纤维、亚麻布纤维、黄麻纤维、剑麻纤维、丝纤维、丝线、焦麻纤维和/或它们的混合物。

3、根据权利要求 1 或 2 所述的聚乳酸/天然纤维复合材料，其特征是所述的天然纤维是短纤维，或是长纤维。

4、根据权利要求 1 或 2 所述的聚乳酸/天然纤维复合材料，其特征是所述的天然纤维一般用偶联剂溶液进行表面处理，偶联剂为硅氧烷类、钛酸酯类、硬酯酸类、铝酸酯类或稀土类偶联剂。

5、根据权利要求 4 所述的聚乳酸/天然纤维复合材料，其特征是所述的偶联剂中硅氧烷类为γ-氨丙基三乙氧基硅烷，γ-缩水甘油醚氧丙基三甲氧基硅烷，N-（β-氨乙基）-γ-氨丙基三甲氧基硅烷，N-(N-(β-氨乙基)-β-氨乙基)-γ-氨丙基三甲氧基硅烷；偶联剂钛酸酯类为异丙基二（甲基丙烯酰基）异硬脂酰基钛酸酯；偶联剂硬脂酸类为硬脂酸，硬脂酸钙。

6、根据权利要求 1 所述的聚乳酸/天然纤维复合材料，其特征是所述的抗氧剂是四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇，（3，5-二特丁基-4-羟基苯基）丙酸十八酯，β-（3，5-二特丁基-4-羟基苯基）丙酸环己酯，硫代二丙酸二月桂酯。

7、根据权利要求 1 所述的聚乳酸/天然纤维复合材料，其特征是所述的成核剂为无机矿物或有机成核剂。

8、根据权利要求 1 或 7 所述的聚乳酸/天然纤维复合材料，其特征是所述的



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无机矿物成核剂为滑石粉、白炭黑、蒙脱石或高岭石，有机成核剂为沙林树脂。

9、如权利要求 1 所述的聚乳酸/天然纤维复合材料，其特征是所述的润滑剂为液体石蜡、石蜡、硅油、硬脂酸、硬脂酸钙。

10、一种制备权利要求 1 所述的聚乳酸/天然纤维复合材料的生产方法，其特征是所述的生产方法包括下列步骤：

① 将 5～40 份天然纤维浸泡在偶联剂溶液中 0.5~3 小时，之后将其取出并干燥。

② 将 60～95 份聚乳酸树脂、0～1 份抗氧剂、0～2 份成核剂和 0～1 份润滑剂混合后输送到挤出机中，相应的短天然纤维通过侧进料装置加入到挤出机中，而长纤维（纱线）则从排气口或专门的加料口直接加入到挤出机中，进行熔融挤出造粒，制得聚乳酸/天然纤维复合材料。



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# 聚乳酸/天然纤维复合材料及其生产方法

**技术领域：**

本发明属于高分子材料领域，具体涉及一种天然纤维增强改性聚乳酸复合材料及其生产方法。

**背景技术：**

聚乳酸(PLA)在自然界并不存在，是以农业经济作物(玉米、小麦、马铃薯等)的发酵产物乳酸为基本原料制备得来的一种环境友好的材料。聚乳酸具有良好的生物降解性能，同时又具有良好的生物相容性和生物可吸收性，对人体无毒无害，在体内及自然环境中逐渐降解，最终成为二氧化碳和水，不会遗留任何环保问题。所以聚乳酸在很多领域被认为是最具潜力和最有前途的可降解高分子材料。但是纯聚乳酸的某些机械力学性能如耐热性（热变形温度）太低，通常不能满足使用的要求。并且聚乳酸结晶速率很慢，用作注塑件使用时成型周期太长，难以满足成型方面的要求。纤维改性聚乳酸是一种有效的改善材料性能的方法，所得的复合材料具有优异的性能，尤其是天然纤维，优点更加突出。经天然纤维增强改性的聚乳酸机械力学性能、结晶性能和成型加工性等性能都得到大幅改善，同时又不会降低其生物降解性能。

纤维增强改性聚乳酸的研究已经引起了广泛的关注。中国专利（申请号94192896.9）公开了一种天然纤维增强的热塑性淀粉、纤维素衍生物、聚己内酯、疏水蛋白质或聚乙烯醇；中国专利（申请号01107011.0）公开了一种纤维增强的聚乳酸复合物，采用甲壳素纤维、明胶蛋白纤维、改性人发角蛋白纤维、改性纤维素或聚酰亚胺纤维来改善聚乳酸的强度；中国专利（申请号02113309.3）公开了用聚磷酸钙纤维增强改性聚 L-丙交酯；中国专利（申请号 03117708.5）公开了一种无机填料增强改性的聚 DL-乳酸材料，其中填料包括聚磷酸钙、羟基磷灰石、碳酸钙或氧化锆，该材料保持了聚乳酸良好的生物相容性，而且强度还有显著的提高。但上述发明均存在操作复杂，对机械设备要求高，生产效率低，不易工业化的缺点。

**发明内容：**

本发明的目的在于提供一种具有较好的力学性能，较高的耐热性和改善了



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的成型加工性的聚乳酸/天然纤维复合材料。

本发明的另一个目的在于提供上述聚乳酸/天然纤维复合材料的生产方法。

本发明的技术解决方案是：

聚乳酸/天然纤维复合材料，由60～95份聚乳酸、5～40份天然纤维、0～1份抗氧剂、0～2份成核剂、0～1份润滑剂组成。

本发明天然纤维包括大麻纤维、棉纤维、竹纤维、苎麻纤维、亚麻纤维、亚麻布纤维、黄麻纤维、剑麻纤维、丝纤维、丝线、焦麻纤维和/或它们的混合物。天然纤维可以是短纤维，也可以是长纤维（纱线）。天然纤维的表面一般用偶联剂进行处理。偶联剂为硅氧烷类，如γ-氨丙基三乙氧基硅烷，γ-缩水甘油醚氧丙基三甲氧基硅烷，N-（β-氨乙基）-γ-氨丙基三甲氧基硅烷，N-(N-(β-氨乙基)-β-氨乙基)-γ-氨丙基三甲氧基硅烷；钛酸酯类，如异丙基二（甲基丙烯酰基）异硬脂酰基钛酸酯；硬脂酸类，如硬脂酸，硬脂酸钙；其它种类还可以为铝酸酯类和稀土类偶联剂等。

本发明中加入抗氧剂的目的是为了降低在制备复合材料的过程中聚乳酸的降解及氧化。加入成核剂的目的是为了提高聚乳酸的结晶速率，改善制品的成型加工性。同时，为了提高复合材料的加工性，可在配方中加入相应的润滑剂。抗氧剂可以是：四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇，（3，5-二特丁基-4-羟基苯基）丙酸十八酯，β-（3，5-二特丁基-4-羟基苯基）丙酸环己酯，硫代二丙酸二月桂酯等。成核剂包括无机矿物如滑石粉、白炭黑、蒙脱石或高岭石等，也可以是有机成核剂如Dupont公司的沙林树脂（Surlyn®）等。润滑剂为液体石蜡、石蜡、硅油、硬脂酸、硬脂酸钙等。

聚乳酸/天然纤维复合材料的生产方法，包括下列步骤：

① 将5～40份天然纤维浸泡在偶联剂溶液中0.5~3小时，之后将其取出并干燥。

② 将60～95份聚乳酸树脂、0～1份抗氧剂、0～2份成核剂和0～1份润滑剂混合后输送到挤出机中，相应的短天然纤维通过侧进料装置加入到挤出机中，而长纤维（纱线）则从排气口或专门的加料口直接加入到挤出机中，进行熔融挤出造粒，制得聚乳酸/天然纤维复合材料。

本发明方法具有操作简单、生产效率高等优点，制备的聚乳酸/天然纤维复



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合材料，具有较高的模量及耐热性，以及较好的成型加工性，同时又没有损失聚乳酸的可生物降解性，可广泛应用于汽车、建筑和居家装饰等领域。

**具体实施方式：**

实施例 1

准确称取 70 份聚乳酸和 0.3 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇混合均匀后从主料斗加入到挤出机中，同时将 30 份苎麻短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品。其力学性能见表一中 1"所示，为了对比，表一中 0"列出了纯聚乳酸的力学性能。

用差示扫描量热法（DSC）测量了复合材料的结晶性能，取第一次降温和第二次升温曲线，用结晶峰的峰值（结晶温度）和半峰宽的大小表征结晶速率，结晶温度越高，半峰宽越窄则结晶速率越大。而结晶峰面积（结晶焓）和熔融峰的面积（熔融焓）表示相对结晶度的大小，焓越大则相对结晶度越高。其结晶性能见表二中 1 * 所示，同时表二中 0 * 列出了纯聚乳酸的结晶性能。

由表一可见：本发明复合材料的力学性能如弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 2

棉短纤维用偶联剂γ-缩水甘油醚氧丙基三甲氧基硅烷进行表面处理，具体方法如下：配制 1wt%的偶联剂水溶液，滴加一定量的浓盐酸调节溶液 PH 3～4，将棉纤维浸泡在溶液中，浸泡处理两小时后取出置于鼓风烘箱中 80°C 烘干。

准确称取 90 份聚乳酸和 0.3 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇混合均匀后从主料斗加入到挤出机中，同时将 10 份处理过的棉短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1，其力学性能见表一中 2"所示，结晶性能见表二中 2 * 所示。

由表一可见：本发明复合材料的力学性能如弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 3

苎麻短纤维用偶联剂γ-缩水甘油醚氧丙基三甲氧基硅烷进行表面处理，浸



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泡时间为 0.5 小时。具体处理方法同实施例 2 中棉纤维的处理。

准确称取 80 份聚乳酸和 0.2 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇混合均匀后从主料斗加入到挤出机中，同时将 20 份处理过的苎麻短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1，其力学性能见表一中 3"所示，结晶性能见表二中 3＊所示。

由表一可见：本发明复合材料的力学性能如弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 4

苎麻短纤维的处理同实施例 2。

准确称取 70 份聚乳酸和 0.2 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇混合均匀后从主料斗加入到挤出机中，同时将 30 份处理过的苎麻短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1，其力学性能见表一中 4"所示,结晶性能见表二中 4＊所示。

由表一可见：本发明复合材料的力学性能如弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 5

大麻短纤维用偶联剂 N-（β-氨乙基）-γ-氨丙基三甲氧基硅烷进行表面处理，浸泡时间为 3 小时。

准确称取 80 份聚乳酸、0.2 份抗氧剂（3，5-二特丁基-4-羟基苯基）丙酸十八酯和 0.5 份成核剂滑石粉，混合均匀后从主料斗加入到挤出机中，同时将 20 份处理过的大麻短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1，其力学性能见表一中 5"所示，结晶性能见表二中 5＊所示。

由表一可见：本发明复合材料的力学性能如弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 6



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亚麻布纤维用偶联剂 N-(N-(β-氨乙基)-β-氨乙基)-γ-氨丙基三甲氧基硅烷进行表面处理，浸泡时间为 2.5 小时。

准确称取 80 份聚乳酸、0.2 份抗氧剂（3，5-二特丁基-4-羟基苯基）丙酸十八酯和 0.5 份成核剂蒙脱石，混合均匀后从主料斗加入到挤出机中，同时将 20 份处理过的亚麻布纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1，其力学性能见表一中 6#所示，结晶性能见表二中 6 * 所示。

由表一可见：本发明复合材料的力学性能如拉伸强度、弯曲强度、弯曲模量等均比纯聚乳酸的性能好很多。

由表二可见：本发明的结晶性能也明显优于纯聚乳酸的结晶性能。

实施例 7

准确称取 92 份聚乳酸和 0.3 份抗氧剂（3，5-二特丁基-4-羟基苯基）丙酸十八酯，混合均匀后从主料斗加入到挤出机中，同时将 8 份苎麻长纤维（纱线）通过挤出机前端进料口（排气口）直接加入挤出机中挤出造粒，干燥后制得产品，其力学性能见表一中 7#所示。

由表一可见：本发明复合材料的力学性能如拉伸强度、弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

实施例 8

准确称取 84 份聚乳酸和 0.3 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇，混合均匀后从主料斗加入到挤出机中，同时将 16 份苎麻长纤维（纱线）通过挤出机前端进料口（排气口）直接加入挤出机中挤出造粒，干燥后制得产品，其余同实施例 7，其力学性能见表一中 8#所示。

由表一可见：本发明复合材料的力学性能如拉伸强度、弯曲强度、弯曲模量和热变形温度等均比纯聚乳酸的性能好很多。

表一 聚乳酸/天然纤维复合材料的力学性能

| 性能 / 样品号 | 拉伸强度/MPa | 弯曲强度/MPa | 弯曲模量/GPa | Izod 缺口冲击强度（kJ/m$^2$,23℃） | 热变形温度(℃, 1.8MPa) |
|---|---|---|---|---|---|



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| | | | | | |
|---|---|---|---|---|---|
| 0# | 64 | 73 | 4.0 | 3.7 | 61 |
| 1# | 57 | 91 | 7.4 | 2.4 | 127 |
| 2# | 62 | 81 | 5.4 | 2.8 | 77 |
| 3# | 62 | 96 | 6.9 | 2.7 | 119 |
| 4# | 69 | 103 | 8.2 | 2.7 | 136 |
| 5# | 64 | 100 | 7.1 | 2.9 | 121 |
| 6# | 63 | 96 | 7.1 | 2.7 | 120 |
| 7# | 72 | 98 | 5.4 | 2.8 | 65 |
| 8# | 77 | 107 | 6.6 | 3.2 | 101 |

表二 聚乳酸/天然纤维复合材料的结晶性能

| 性能 / 样品号 | 结晶温度 /(℃) | 结晶焓 (J/g) | 半峰宽 /(℃) | 熔融温度 /(℃) | 熔融焓 (J/g) |
|---|---|---|---|---|---|
| 0 * | 93.5 | 4.6 | 15.4 | 169.8 | 40.8 |
| 1 * | 95.4 | 13.1 | 14.1 | 168.1 | 42.5 |
| 2 * | 94.6 | 7.2 | 15.1 | 168.3 | 43.5 |
| 3 * | 94.6 | 7.5 | 14.5 | 168.6 | 46.3 |
| 4 * | 96.4 | 17.6 | 13.9 | 168.5 | 47.6 |
| 5 * | 110.4 | 35.3 | 6.6 | 170.4 | 41.1 |
| 6 * | 96.2 | 18.6 | 12.6 | 162.5 | 46.3 |

实施例 9

丝短纤维用偶联剂异丙基二（甲基丙烯酰基）异硬脂酰基钛酸酯进行表面处理。

准确称取 60 份聚乳酸、0.5 份抗氧剂β-（3，5-二特丁基-4-羟基苯基）丙酸环己酯、2 份成核剂白炭黑和 1 份润滑剂硬脂酸，混合均匀后从主料斗加入到挤出机中，同时将 40 份处理过的丝短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1。

实施例 10



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剑麻短纤维用偶联剂硬脂酸进行表面处理。

准确称取 60 份聚乳酸、0.5 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇、2 份成核剂高岭石和 1 份润滑剂硬脂酸钙，混合均匀后从主料斗加入到挤出机中，同时将 40 份处理过的剑麻短纤维通过侧进料装置加入到挤出机中进行挤出造粒，干燥后制得产品，其余同实施例 1。

实施例 11

准确称取 60 份聚乳酸、1 份抗氧剂四{β-（3，5-二特丁基-4-羟基苯基）丙酸}季戊四醇、0.5 份成核剂白炭黑和 0.5 份润滑剂液体石蜡，混合均匀后从主料斗加入到挤出机中，同时将 40 份大麻（也可以是苎麻、亚麻、棉、竹、黄麻、剑麻、丝、焦麻和/或它们的混合物）长纤维（纱线）通过挤出机前端进料口（排气口）直接加入挤出机中挤出造粒，干燥后制得产品，其余同实施例 7。

实施例 12

准确称取 70 份聚乳酸和 0.5 份抗氧剂硫代二丙酸二月桂酯混合均匀后从主料斗加入到挤出机中，同时将 30 份竹长纤维（纱线）通过挤出机前端进料口（排气口）直接加入挤出机中挤出造粒，干燥后制得产品，其余同实施例 7。



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**Patent/Publication: CN101003667A Polylactic/ natural fiber composites and its producing method**

## Bibliography

**DWPI Title**
Polylactic/ natural fiber composites and its producing method

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Polylactic/ natural fiber composites and its producing method

**Assignee/Applicant**
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Original: Dongli Fibrin Research Institute ( China ) Co. Ltd.

**Inventor**
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## Abstract

**Abstract**

The invention claims a polylactic/ natural fiber composite, it consists of polylactic resin and natural fiber. The producing method of the composite includes: disposing the surface of the natural fiber by coupling agents; and mixing the natural fiber with polylactic resin, antioxidant, nucleater and lubricant. The product is made by melting and extruding the pellet. The invention has simple manipulation and high producing efficiency. The polylactic/ natural fiber composite have high modulus, heat-resisting and good capability of moulding. It keeps the biodeqradability of the polylactic and can be used in the field of vehicle, construction and home decoration.

## Classes/Indexing

**IPC**

| Current IPC-R | Invention | Version | Additional | Version |
|---|---|---|---|---|
| Advanced | C08L 67/04<br>B29C 47/00<br>C08J 3/12<br>C08J 5/06 | 20060101<br>20060101<br>20060101<br>20060101 | - | - |
| Core | C08L 67/00<br>B29C 47/00<br>C08J 3/12<br>C08J 5/04 | 20060101<br>20060101<br>20060101<br>20060101 | - | - |
| Subclass | - | - | - | - |

| Original IPC-R | Invention | Version | Additional | Version |
|---|---|---|---|---|
| Advanced | C08L 67/04<br>B29C 47/00<br>C08J 3/12<br>C08J 5/06 | 20060101<br>20060101<br>20060101<br>20060101 | - | - |
| Core | B29C 47/00<br>C08J 3/12<br>C08J 5/04<br>C08L 67/00 | 20060101<br>20060101<br>20060101<br>20060101 | - | - |
| Subclass | - | - | - | - |



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**ECLA**
C08J 5/06+L67/04 C08J 5/04K+L67/04

**DWPI Manual Codes**

Expand DWPI Manual Codes

## Legal Status

**INPADOC Legal Status**

| Gazette Date | Code | Description |
|---|---|---|
| 2009-09-30 | C02 - | DEEMED WITHDRAWAL OF PATENT APPLICATION AFTER PUBLICATION (PATENT LAW 2001) |
| 2007-07-25 | C06 + | PUBLICATION |

Get Family Legal Status

## Family

**Family**

INPADOC Family (1)

| | Publication Number | Publication Date | Inventor | Assignee/Applicant | Title |
|---|---|---|---|---|---|
| | CN101003667A_ | 2007-07-25 | DONG Wei-wei | DONGLI FIBER INST CHINA CO LTD | Composite material of poly lactic acid / natural faric |

## Description

No Description exists for this Record

## Citations

**Citation**

Expand Citing Patents (1)

Cited Patents (0)

Cited Non-patents (0)

## Other

**Attorney / Agent**
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# (54) BIODEGRADABLE LAMINATE SHEET AND MOLDED ITEM FROM BIODEGRADABLE LAMINATE SHEET

(57) A biodegradable laminate sheet having as its object to provide a formed body superior in heat resistance, shock resistance, transparency and formability, and having non-stretched polylactic acid-family resin layer of which the crystallinity is 20% or less, and a layer comprising a biodegradable resin other than a polylactic acid-family resin.

EP 1 541 345 A1

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## Description

Technical Field

**[0001]** The present invention relates to a biodegradable laminate sheet of a polylactic acid-family resin which can be formed by various formings such as vacuum forming, air-pressure forming, vacuum air-pressure forming and press forming, a method of forming such a laminate sheet, and a formed body obtained from such a laminate sheet. More specifically, it relates to a biodegradable laminate sheet of a polylactic acid-family resin which is superior in heat resistance, shock resistance and formability, and which decomposes under a natural environment, a method of forming such a laminate sheet, and a formed body obtained from such a laminate sheet such as a food container such as a cup or a tray, a blister packaging material, a hot-fill container, a plastic case, or a tray or a carrier tape for transporting electronic parts.

Background art

**[0002]** As a material for a food container such as a cup or a tray, a blister pack, a container for hot-fill, a plastic case, or a tray or a carrier tape for transporting electronic parts, polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, or the like have been used. These plastic products or the like are generally discarded after use, so that disposal such as burning and burial when discarding after use poses a problem. Resins such as polyethylene, polypropylene and polystyrene are large in calorific value when burnt, so that they may damage incinerators during burning treatment, and polyvinyl chloride produces harmful gas during burning.

**[0003]** On the other hand, for burial disposal, too, since these plastic products are high in chemical stability, they will barely decompose in the natural environment and remain semipermanently in the earth, so that they will saturate the capacity of garbage disposal sites in a short time. Also, if discarded in the natural environment, they will mar the landscape or destroy the life environment of marine lives or the like.

**[0004]** Therefore, from the viewpoint of environmental protection, in recent years, studies and developments of biodegradable materials are being actively done. As one of biodegradable materials that are gathering attention, there is a polylactic acid. Since a polylactic acid-family resin is biodegradable, hydrolysis proceeds naturally in the earth and water, so that it becomes a harmless decomposed product. Also, since it is small in burning calorie, even if it is subjected to burning treatment, it will not damage furnaces.

**[0005]** Further, since the starting material originates from a plant, it does not resort to oil resources which is exhausting.

**[0006]** But a polylactic acid-family resin is low in heat resistance, and was not suitable for use at high temperature such as containers for heated foods or containers into which hot water is to be poured. Also, in storing or transporting polylactic acid-family resin sheets or their formed bodies, the interiors of storages, transporting trucks and ships often reach high temperature in summer, so that problems of deformation, fusing, etc. occur.

**[0007]** As a technique for imparting heat resistance to a polylactic acid-family resin, there is a method in which in a forming step, the heat resistance is imparted by crystallizing a polylatic acid to a high degree in a mold by holding the mold near the crystallizing temperature of the polylactic acid-family resin (80-130°C). But in this method, in order to crystallize the formed polylactic acid in the mold, until crystallization is completed, the formed body has to be held in the mold, so that the forming cycle becomes longer than during normal forming, and thus the manufacturing cost becomes high. Also, since it is necessary to heat the mold, a heating facility is also necessary.

**[0008]** Also, there is a method in which heat resistance is imparted by post-crystallizing a polylactic acid-family resin to a high degree by annealing it after forming. But in this method, in the process of post-crystallizing the formed body of a polylactic acid-family resin, the formed body may be deformed, so that problems arise in dimensional accuracy. Also, since a step for post-crystallizing is necessary, the manufacturing cost becomes high.

**[0009]** As another method of imparting heat resistance to a polylactic acid-family resin, there is known a method in which after making the storage elasticity in a predetermined range by pre-crystallizing a lactic acid-family polymer sheet by annealing, forming is carried out in a heated mold (see patent document 1). But in this method, too, in order to obtain a heat-resistant formed body, it is necessary to keep the temperature of the mold near the crystallizing temperature of the polylactic acid-family resin (80-130°C), and finish crystallization of the polylactic acid-family resin in the mold, so that a facility for heating the mold is necessary. Also, in this method, the forming cycle becomes longer than during normal forming, so that the manufacturing cost becomes high.

**[0010]** Furhter, in the above-described method in which a polylactic acid-family resin is crystallized, the formed body obtained by the growth of spherutiles basically becomes opaque. Thus it is difficult to obtain a formed body having transparency.

**[0011]** On the other hand, as a technique regarding laminate sheets comprising a polylactic acid-family resin and a biodegradable aliphatic polyester other than a polylactic acid-family resin; there are known laminate films of aliphatic



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polyester having a number-average molecular weight of 10000 or over and polylactic acid-family resin (see patent document 2), and laminate films of polylactic acid-family resin and a biodegradable aliphatic polyester other than polylactic acid-family resin (see patent document 3).

(patent document 1) JP patent publication 8-73628
(patent document 2) JP patent publication 8-85194
(patent document 3) JP patent publication 10-6445

Problem that the Invention Intends to Solve

**[0012]** But polylactic acid-family resin used as laminate films described in the patent documents 2 and 3 are stretched ones, and the technical object is to improve the heat-sealability of packaging bags.

**[0013]** Therefore, the present invention has as its object to provide a formed body which is superior in heat resistance, shock resistance, transparency and formability.

Means to solve the object

**[0014]** As a result of conducting vigorous consideration to solve the above object, it has been found out that by laminating a polylactic acid-family resin and a biodegradable resin other than a polylactic acid-family resin, various formings such as vacuum forming, air-pressure forming, vacuum air-pressure forming and press forming are possible, and also a heat-resistant formed body is obtainable even without holding the mold near the crystallizing temperature of the polylactic acid-family resin (80-130°C), and the present invention has been reached.

**[0015]** The invention concerning the biodegradable laminate sheet according to the present application relates to a sheet having a non-stretched polylactic acid-family resin of which the crystallinity is 20% or less and a biodegradable resin layer other than a polylactic acid-family resin.

**[0016]** Further, as the biodegradable resin layer other than a polylactic acid-family resin, a biodegradable aliphatic polyester layer other than a polylactic acid-family resin of which the glass transition temperature is 0°C or less and which has the melting point of 80°C or over may be used.

**[0017]** Also, it may be formed of at least three layers, with the biodegradable resin layers other than a polylactic acid-family resin forming outer layers, and the non-stretched polylactic acid-family resin layer being at least one layer sandwiched between the outer layers.

**[0018]** Further, it may be formed of at least three layers, with the non-stretched polylactic acid-family resin being outer layers, and the biodegradable resin layers other than a polylactic acid-family resin being at least one layer sandwiched between the outer layers.

**[0019]** Also, the non-stretched polylactic acid-family resin and the biodegradable resin layer other than a polylactic acid-family resin can be laminated by co-extrusion.

**[0020]** Further, the biodegradable laminate sheet described above may be formed at a temperature equal to or higher than the melting point of the biodegradable resin other than a polylactic acid-family resin.

Best Mode for Embodying the Invention

**[0021]** Below, embodiments of the present invention are described.

**[0022]** The biodegradable laminate sheet according to the present invention is a laminate sheet having a layer comprising a non-stretched polylactic acid-family resin of which the crystallinity is 20% or less, and a layer comprising a biodegradable resin other than a polylactic acid-family resin.

**[0023]** The polylactic acid-family resin used in the present invention comprises a polylactic acid-family polymer. The polylactic acid-family polymer includes a homo-polymer of which the structural unit is L-lactic acid or D-lactic acid, i.e. poly (L-lactic acid) or poly (D-lactic acid), a copolymer of which the structural unit is both of L-lactic acid and D-lactic acid, i.e. poly (DL-lactic acid), or their mixture. Further, it may be $\alpha$-hydroxy carboxylic acid or a copolymer of diol/dicarboxylic acid.

**[0024]** As a polymerizing method for a polylactic acid-family polymer, any known methods such as condensation polymerization or ring-opening polymerization may be used. For example, in a condensation polymerization, it is possible to obtain a polylactic acid-family polymer having an arbitrary composition by directly dehydro-condensation - polymerizing L-lactic acid, D-lactic acid or their mixture.

**[0025]** Also, in a ring-opening polymerization, a polylactic acid-family polymer is obtainable by polymerizing a lactide, which is a cyclic dimer of lactic acid, while using a polymerization adjusting agent as necessary, using a selected catalyst. Among lactides, there are L-lactide, which is a dimer of L-lactic acid, D-lactide, which is a dimer of D-lactic acid, and DL-lactide, which comprises L-lactic acid and D-lactic acid. By polymerizing them while mixing as necessary, a polylactic acid-family polymer having an arbitrary composition and crystallinity is obtainable.



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**[0026]** Further, for example, if it is necessary to improve heat resistance, as small-amount copolymerizing components, a non-aliphatic dicarboxylic acid such as terephthalic acid, or a non-aliphatic diols such as ethylene oxide addition products of bisphenol A may be used.

**[0027]** Still further, for the purpose of increasing the molecular weight, a small amount of a chain extender such as a diisocyanate compound, an epoxy compound or an acid anhydride may be used.

**[0028]** As the other hydroxyl-carboxylic acid units to be copolymerized with the polylactic acid-family polymer, an optical isomer of lactic acid (D-lactic acid for L-lactic acid, L-lactic acid for D-lactic acid), bifunctional aliphatic hydroxylcarboxylic acids such as glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxy-n-butyric acid, 2-hydroxy 3,3-dimethyl butyric acid, 2-hydroxy 3-methylbutyric acid, 2-methyllactic acid, and 2-hydroxycaproic acid, and lactones such as caprolactone, butyrolactone and valerolactone may be used.

**[0029]** As the aliphatic diol to be copolymerized with the polylactic acid-family polymer, ethylene glycol, 1,4-butane diol, 1,4-cyclohexane dimethanol or the like can be used. Also, as the aliphatic dicarboxylic acid, succinic acid, adipic acid, suberic acid, sebacic acid, dodecanoic diacid, or the like can be used.

**[0030]** But as for the composition ratio in the polylactic acid-family resin, the polylactic acid is the main body, and the molar % of lactic acid is 50 molar % or over.

**[0031]** The preferable range of the weight-average molecular weight of the polylactic acid-family polymer is from 50000 to 400000, preferably form 100000 to 250000. If it is below this range, practicality will scarcely reveal. If it exceeds, the melt viscosity would be too high, so that formability is inferior.

**[0032]** The biodegradable resin other than a polylactic acid-family resin is a constituent component for imparting heat resistance and shock resistance to the biodegradable laminate sheet and its formed body of the present invention.

**[0033]** As the biodegradable resin other than a polylactic acid-family resin, polyesteramide-family resin, cellulose-family resin, biodegradable aliphatic-family polyester other than a polylactic acid-family resin, polyvinyl alcohol, polyurethane, or the like can be used.

**[0034]** As the polyester amide-family resin, a copolymer of caprolactone and caprolactum can be used. Also, as the cellulose-family resin, cellulose acetate or the like can be cited.

**[0035]** As the biodegradable aliphatic-family polyester other than a polylactic acid-family resin, polyhydroxy carboxylic acid, aliphatic polyester or aliphatiec aromatic polyester obtained by condensing aliphatic diol and aliphatic dicarboxylic acid or aromatic dicarboxylic acid; aliphatic polyester copolymer obtained from aliphatic diol and aliphatic dicarboxylic acid and hydroxycarboxylic acid; aliphatic polyesters obtained by ring opening polymerizing cyclic lactones; synthetic aliphatic polyesters; and aliphatic polyesters bio-synthesized in fungus bodies may be used.

**[0036]** As the polyhydroxy carboxylic acid, a homopolymer or a copolymer of hydroxycarboxylic acids such as 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxy-n-butyric acid, 2-hydroxy-3,3-dimethylebutyric acid, 2-hydroxy-3-methylbutyric acid, 2-methyllactic acid or 2-hydroxycaproic acid may be used.

**[0037]** As the aliphatic diol, ethylene glycol, 1,4-butane diol, 1,4-cyclohexane dimethanol or the like may be used. Also, as the aliphatic dicarboxylic acid, succinic acid, adipic acid, suberic acid, sebacic acid, dodecanoic diacid, or the like may be used.

**[0038]** As the aromatic dicarboxylic acid, terephthalic acid, isophthalic acid or the like may be used.

**[0039]** The aliphatic polyester obtained by condensing these aliphatic diols and aliphatic dicarboxylic acids, and the aliphatic aromatic polyester obtained by condensing aliphatic diols, aliphatic dicarboxylic acids and aromatic dicarboxylic acids are obtained by selecting one or more kind from these compounds, and condensation polymerizing them. Further, as necessary, by jumping-up with an isocyanate compound, a desired polymer can be obtained.

**[0040]** As aliphatic diols and aliphatic carboxylic acids used for an aliphatic polyester copolymer obtained from aliphatic diols and aliphatic dicarboxylic acids and hydroxycarboxylic acids, ones mentioned above may be used. Also, as hydroxycarboxylic acids, L-lactic acid, D-lactic acid, DL-lactic acid, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxy-n-butyric acid, 2-hydroxy 3,3-dimetyl butyric acid, 2-hydroxy 3-methyl butyric acid, 2-methil lactic acid, 2-hydroxy caproic acid or the like may be used. For example, polybutylene succinate lactic acid, polybutylene succinate adipate lactic acid or the like may be used.

**[0041]** But as for the composition ratio in this case, aliphatic diol and aliphatic dicarboxylic acid are main bodies. For the molar %, aliphatic diol: 35-49.99 mole %, aliphatic dicarboxylic 35-49.99 mole %, and hydroxylcarboxylic acid: 0.02-30 mole %.

**[0042]** The aliphatic polyester obtained by ring opening polymerizing a cyclic lactone is obtained by polymerizing, as a cyclic monomer, one or more kind of ε-caprolactone, δ-valerolactone, β-methyl-δ-valerolactone.

**[0043]** As the synthetic-family aliphatic polyester, a copolymer of a cyclic anhydride with an oxirane such as a copolymer of anhydrous succinic acid with ethylene oxide or propylene oxide may be used.

**[0044]** As the aliphatic polyester biosynthesized in the fungus, an aliphatic polyester biosynthesized by acetyl coenzyme A (acetyl CoA) in fungus represented by Alcaligenes eutrophus can be cited. The aliphatic polyester biosynthesized in the fungus is mainly poly-β-hydroxybutyric acid (poly3HB). But in order to improve practical properties as a plastic, it is industrially advantageous to copolymerize hydroxyvaleric acid (HV) into a copolymer of poly(3HB-CO-



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3HV). The HV copolymerization ratio is generally preferably 0-40 mol%. Further, instead of hydroxyvaleric acid, long-chained hydroxyalkanoate such as 3-hydroxyhexanoate, 3-hydroxyoctanoate, 3-hydroxyoctadecanoate, or the like may be copolymerized.

**[0045]** As specific examples of biodegradable aliphatic-family polyester other than a polylactic acid-family resin, at least one kind selected from the group consisting of polybuthylene succinate, polybutylene succinate adipate, polybutylene adipate terephthalate, polybutylene succinate adipate terephthalate, polybutylene succinate lactic acid, polybutylene succinate adipate lactic acid, polyester carbonate, a copolymer of polyhydroxybutyrate and polyhydroxyvalerate, and a copolymer of polyhydroxybutyrate and polyhydroxyhexanoate can be cited.

**[0046]** The crystallinity of non-stretched polylactic acid-family resin which is a constituent component of one layer of the biodegradable laminate sheet according to the present invention, is preferably 20% or less, more preferably, 15% or less and further preferably 10% or less.

**[0047]** The method of suppressing the crystallinity of the non-stretched polylactic acid-family resin to 20% or less is not particularly limited. But for example, a method in which a sheet extruded by an extruder is cooled by a cooling roll such as a casting roll (at a temperature of 15-60°C) to suppress crystallization of the polylactic acid-family resin, and a method in which the rate of D-lactic acid and L-lactic acid in the polylactic acid-family resin is adjusted and because a random copolymer in which the rate of L-lactic acid and D-lactic acid is about 95:5 to 5:95 is low in crystallinity, such polylactic acid-family polymers may be used.

**[0048]** If the crystallinity of the non-stretched polylactic acid-family resin layer exceeds 20%, formability worsens. Thus general purpose forming such as vacuum forming or air-pressure forming becomes difficult. Also, if the crystallinity exceeds 20%, due to the growth of spherulites of the polylactic acid-family resin, the transparency will worsen.

**[0049]** For the crystallinity of the polylactic acid-family resin, its lower limit is not limited if it is 20% or less.

**[0050]** The polylactic acid-family resin layer is preferably a non-stretched one. If a sheet obtained by stretching a polylactic acid-family resin is used, in order to obtain a formed body, excessive pressure of e.g. about 9 $kg/cm^2$ is necessary, so that forming at low pressure such as vacuum forming will be difficult. Also, since a stretched sheet needs an extra step of stretching compared to a non-stretched one, it is disadvantageous in cost too.

**[0051]** The glass transition temperature of the biodegradable resin other than a polylactic acid-family resin which is a constituent component of the other layer of the biodegradable laminate sheet according to the present invention is preferably 0°C or lower, and more preferably -20°C or lower. If high than 0°C, the improvement in the shock resistance is insufficient. Also, the lower limit of the glass transition temperature is not particularly limited, but is preferably practically -60°C or more. With a material of which the glass transition temperature is lower than -60°C, the melting point will be lower than 80°C, so that the heat resistance may be insufficient.

**[0052]** Also, the melting point of the biodegradable resin other than a polylactic acid-family resin has to be 80°C or over. If the melting point is less than 80°C, the heat resistance of the formed body may be insufficient. Also, the upper limit of the melting point is not particularly limited, but from the viewpoint of formability, it is preferably 170°C.

**[0053]** The layer comprising the biodegradable resin other than a polylactic acid-family resin may be a stretched one or a non-stretched one, but as described above, from the cost aspect, a non-stretched one is preferable.

**[0054]** The thickness of the biodegradable laminate sheet of the present invention is not particularly limited, if it has such a thickness that it can be used for a normal heat forming technique. But normally, the total thickness is preferably in the range of 0.07-2.0 mm.

**[0055]** Also, the ratio of the thickness of the layer comprising the biodegradable resin other than a polylactic acid-family resin to the thickness of all the layers is 0.005-0.7. Specifically, the thickness of the layer comprising the biodegradable resin other than a polylactic acid-family resin is preferably 0.003-0.1 mm, more preferably 0.005-0.05 mm.

**[0056]** The thickness of the layer of a polylactic acid-family resin is a thickness obtained by subtracting the thickness of the layer comprising the biodegradable resin other than a polylactic acid-family resin from the total thickness.

**[0057]** The biodegradable laminate sheet of the present invention will do if it contains at least two layers, i.e. a non-stretched polylactic acid-family resin layer and a layer comprising the biodegradable resin other than a polylactic acid-family resin.

**[0058]** Further, if the biodegradable laminate sheet of the present invention is formed of at least three layers, one layer is outer layers, and the other layer is at least one layer sandwiched by the outer layers. Specifically, the layer comprising the biodegradable resin other than a polylactic acid-family resin forms the outer layers, and the non-stretched polylactic acid-family resin layer is at least one layer sandwiched by the outer layers, or alternatively the non-stretched polylactic acid-family resin is the outer layers, and the layer comprising the biodegradable resin other than a polylactic acid-family resin may be at least one layer sandwiched by both of the outer layers.

**[0059]** Also, so long as the object of the present invention is not impaired, end materials produced during the manufacturing process may be mixed in the other layer for recycling.

**[0060]** The method of manufacturing the biodegradable laminate sheet of the present invention is not particularly limited if the object of the present invention is not impaired. But for example, ① a coextrusion method in which the polylactic acid-family layer and the layer comprising a biodegradable resin other than a polylactic acid-family resin are



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laminated with a multi-manifold type or field block type base using two or three or more extruders to extrude as a molten sheet, ② a method in which the one layer, which has been rolled out, is coated with the other resin, and ③ a method in which the layers, which are at suitable temperatures, are hot-pressed using a roll or press, and ④ a method in which they are stuck together using an adhesive can be cited. But in view of ease of the manufacturing and the cost, the coextrusion method is preferable.

**[0061]** The forming temperature for the biodegradable laminate sheet is preferably the melting point of the biodegradable resin other than a polylactic acid-family resin or higher. If less than the melting point, the heat resistance and formability may be insufficient.

**[0062]** By forming the biodegradable laminate sheet according to the present invention by an arbitrary method such as by using a forming mold, a formed body is obtainable. As examples of the formed body, there are lunchboxes, trays and cups for foods such as fresh fish, meat, fruits and vegetables, bean curds, household dishes, desserts and instant noodles; packaging containers for toothbrushes, batteries, drugs, cosmetics, etc.; hot-fill containers for puddings, jam and curry; plastic cases having fold lines; or trays for transporting electronic parts such as ICs, transistors and diodes; and carrier tapes.

**[0063]** Further, for the biodegradable laminate sheet of the present invention, various modifications are possible by adding secondary additives. As examples of secondary additives, stabilizers, antioxidants, UV absorbers, pigments, antistats, conductive agents, release agents, plasticizers, perfumes, antimicrobials, nucleation agents, and other similar ones can be cited.

Examples

**[0064]** Below, by showing manufacturing examples, examples and comparative examples, the present invention will be described in detail, but the present invention is not limited whatsoever. Physical values in Examples and Comparative Examples were measured and evaluated by the following methods.

♦ Heat resistance

**[0065]** For formed bodies obtained from biodegradable laminate sheets, after carrying out heat treatment for 20 minutes at 80°C using a hot air circulation type oven (FC-610 made by Advantec Toyo Kaisha, Ltd.), they were let to cool to 23±2°C. The heat-treated formed bodies were put in water of 23±2°C with the volume of the water filling the formed bodies made as the volume (internal volume) of the formed bodies. On the other hand, water of 23±2°C was put into formed bodies which were left at 23± 2°C without carrying out heat treatment, and the volume of the water filling the formed body was made as the volume (internal volume) of the formed bodies before heat treatment. Using them, the volume reduction ratio of the formed bodies was calculated from the following formula.

$$\text{Volume reduction ratio} = \{1 - (\text{volume of formed body after heat treatment} / \text{volume of formed body before heat treatment})\} \times 100$$

♦ Shock resistance

**[0066]** Using Hydroshot shock tester Model HTM-1 made by Toyo Seiki Co., Ltd., at temperature 23°C, a firing core having a diameter of 1/2 inch was collided against the biodegradable sheets at a speed of 3 m/sec. and the energy needed to destroy it was calculated.

♦ Crystallizing temperature

**[0067]** Under JIS-K-7121, using differential scanning calorimetry (hereinafter DSC), ΔHm and ΔHc attributable to polylactic acid-family resin in biodegradable sheet were determined at the temperature rising speed of 10°C/min, and the crystallizability of polylactic acid-family resin was calculated by use of the following formula:

$$\text{Cristallinity: xc \%} = (\Delta Hm - \Delta Hc) / (92.8 \times \text{content of polylactic acid-family resin in sheet}) \times 100$$

♦ Melting point

**[0068]** Under JIS-K-712, under differential scanning calorimetry (DSC), the melting point was measured at the tem-



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perature rising speed of 10°C /min.

♦ Formability

**[0069]** Using a forming mold (mold temperature 25°C) of 100 mm dia, depth 30 mm, drawing ratio of 0.3, vacuum forming (vacuum pressure:-70cmHg) was done, and the shape imparting state of the formed bodies was observed.

♦ Haze

**[0070]** Measurements were made under JIS-K-7105.

(Example 1)

**[0071]** 15 ppm of tin octylate was added to 100 kg of L-lactide (trade name: PURASORB L) made by PURAC JAPAN, and the mixture was put in a 500-liter batch type polymerization tank having a stirrer and heater. Nitrogen replacement was carried out, and polymerization was carried out for 60 minutes at 185°C at the stirring speed of 100 rpm. The molten resin obtained was fed into a 40 mm dia. same-direction, two-shaft extruder having vacuum vents in three tiers and made by Mitsubishi Heavy Industries, Ltd. and extruded in strands at 200°C while degassing at a vent pressure of 4 torr to pelletize it, and dried at 70°C for 24 hr. The weight-average molecular weight of the polylactic acid-family resin obtained was 200000, and the L-body content was 99.5%. The melting point measured under DSC was 171°C.
**[0072]** The pellets obtained were fed to a 65 mm dia. single-shaft extruder, and were extruded through a multi-manifold type base at 200°C for an intermediate layer.
**[0073]** Also, simultaneously, dried pellets of polybutylene succinate adipate (BIONOLLE made by Showa Highpolymer Co., Ltd. melting point: 95°C, glass transition temperature: -40°C) as a biodegradable resin other than a polylactic acid-family resin were fed into a 32 mm dia. single-shaft extruder, and were extruded through a multi-manifold type base at 190°C for front and back layers. At this time, the extruding amount was adjusted so that the thickness ratio of the front layer, intermediate layer and back layer would be about 1:28:1.
**[0074]** The extruded molten sheet was brought into contact with a cast roll at 40°C, and a biodegradable laminate sheet 300 microns thick was obtained. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 9%.
**[0075]** Next, using the biodegradable laminate sheet obtained, a formed body was formed. That is, using a forming mold (mold temperature 25°C), vacuum forming was carried out at the sheet temperature of 100°C, vacuum pressure of -70 cmHg to obtain a biodegradable formed body. The formed body obtained was evaluated in heat resistance, shock resistance, formability and haze at 80°C for 20 min. The results thereof are shown in Table 1.

(Example 2)

**[0076]** Except that the thickness ratio of the front layer, intermediate layer and back layer was changed to 1:8:1, a biodegradable laminate sheet was obtained in the same manner as in Example 1. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 8%.
**[0077]** Also, using the biodegradable laminate sheet obtained, a formed body was obtained in the same manner as in Example 1. The formed body obtained was evaluated as in Example 1. The results thereof are shown in Table 1.

(Example 3)

**[0078]** Except that the thickness ratio of the front layer, intermediate layer and back layer was changed to 1:4:1, a biodegradable laminate sheet was obtained in the same manner as in Example 1. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 8%.
**[0079]** Also, using the biodegradable laminate sheet obtained, a formed body was obtained in the same manner as in Example 1. The formed body obtained was evaluated as in Example 1. The results thereof are shown in Table 1.

(Example 4)

**[0080]** The biodegradable resin other than a polylactic acid-family resin used in Example 1 was fed to a 65 mm dia. single-shaft extruder, and extruded through a multi-manifold type base at 190°C for the intermediate layer.
**[0081]** Also, simultaneously, the polylactic acid-family resin used in Example 1 was fed to a 32 mm dia. single-shaft extruder, and extruded through a multi-manifold type base at 200°C for front and back layers. At this time, the extruding amount was adjusted so that the thickness ratio of the front layer, intermediate layer and back layer would be 2.5:1:2.5.



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**[0082]** The extruded molten sheet was brought into contact with a cast roll at 40°C, and a biodegradable laminate sheet 300 microns thick was obtained. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 7%.

**[0083]** Also, using the biodegradable laminate sheet obtained, a formed body was obtained in the same manner as in Example 1. For the formed body obtained, the same evaluations as in Example 1 were carried out. The results thereof are shown in Table 1.

(Example 5)

**[0084]** Except that as the biodegradable resin other than a polylactic acid-family resin, polybutylene succinate (BIONOLLE made by Showa Highpolymer Co., Ltd. melting point: 111°C, glass transition temperature: -40°C) was used, a biodegradable laminate sheet was obtained in the same manner as in Example 1. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 8%.

**[0085]** Also, the biodegradable laminate sheet obtained was subjected to vacuum forming at the sheet temperature of 120°C, and the vacuum pressure: -70cmHg to obtain a biodegradable formed body.

**[0086]** For the formed body obtained, the same evaluations as in Example 1 were carried out. The results thereof are shown in Table 1.

(Example 6)

**[0087]** 15 ppm of tin octylate was added to 90 kg of L-lactide (trade name: PURASORB L) made by PULAC JAPAN, and 10 kg of DL-lactide (trade name: PURASORB DL) made by the same company, and the mixture was put in a 500-liter batch type polymerization tank having a stirrer and a heater. Nitrogen replacement was carried out, and polymerization was carried out for 60 minutes at 185°C at the stirring speed of 100 rpm. The molten article obtained was fed into a 40 mm dia., same-direction, two-shaft extruder having vacuum vents in three tiers and made by Mitsubishi Heavy Industries, Ltd. and extruded in strands at 200°C while degassing at the vent pressure of 4 torr to pelletize it, and dried at 70°C for 24 hr.

**[0088]** The weight-average molecular weight of the polylactic acid-family resin obtained was 200000, and the L-body content was 94.8%. The melting point measured by DSC was 165°C.

**[0089]** Except that the pellets obtained were used, a biodegradable laminate sheet was obtained in the same manner as in Example 1. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 4%.

**[0090]** Also, using the biodegradable laminate sheet obtained, a formed body was obtained in the same manner as in Example 1. For the formed body obtained, the same evaluations as in Example 1 were carried out. The results thereof are shown in Table 1.

(Comparative Example 1)

**[0091]** The polylactic acid-family resin used in Example 1 was fed to a 65 mm dia. single-shaft extruder, and extruded through a base for a single layer at 200°C. The extruded molten sheet was brought into contact with a cast roll of 40°C to obtain a polylactic acid-family resin single sheet 300 microns thick. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 8%.

**[0092]** Also, using the biodegradable laminate sheet obtained, a formed body was obtained in the same manner as in Example 1. For the formed body obtained, the same evaluations as in Example 1 were carried out. The results thereof are shown in Table 1.

(Comparative Example 2)

**[0093]** The biodegradable laminate sheet obtained in Example 1 was subjected to heat treatment in a hot-air oven at 80°C for 24 hours. The crystallinity of the polylactic acid-family resin of the biodegradable laminate sheet obtained was 33%.

**[0094]** Also, using the biodegradable laminate sheet obtained in Example 1, a formed body was obtained in the same manner as in Example 1. For the formed body obtained, the same evaluations as in Example 1 were made. The results thereof are shown in Table 1.

(Comparative Example 3)

**[0095]** For the biodegradable laminate sheet obtained in Example 1, vacuum forming was carried out at a sheet



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temperature of 75°C and vacuum pressure of -70cmHg to obtain a biodegradable formed body.

**[0096]** For the formed body obtained, the same evaluations as in Example 1 was carried out. The results thereof are shown in Table 1.

(Results)

**[0097]** As shown in Table 1, Examples 1-6 were satisfactory in heat resistance, shock resistance and formability, and good results were obtained. For ones in which the rate of the layer comprising the biodegradable resin other than a polylactic acid-family resin was low, transparency was good too.

**[0098]** On the other hand, in Comparative Example 1, since there is no layer comprising a biodegradable resin other than a polylactic acid-family resin, the results were poor in heat resistance and shock resistance.

**[0099]** In Comparative Example 2, since the crystallinity of the polylactic acid-family resin was high, the shape imparting properties of the formed body were insufficient and there was no transparency either.

**[0100]** In Comparative Example 3, since it is formed at a lower temperature than the melting point of the biodegradable resin other than a polylactic acid-family resin, the product showed poor heat resistance, and the shape imparting properties were not sufficient either.

Effect of the invention

**[0101]** As described above, in the present invention, by using a laminate sheet comprising a polylactic acid-family resin and a biodegradable resin other than a polylactic-acid family resin for forming, it is possible to provide a formed body superior in heat resistance, shock resistance, transparency and formability by using a polylactic acid-family which is capable of various formings such as vacuum forming, air-pressure forming, vacuum air-pressure forming and press forming.



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TABLE 1

| | | unit | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| front & back layer | resin | — | B | B | B | A | B | B | A | B | B |
| | thickness | μ | 10 each | 30 each | 50 each | 125 each | 10 each | 10 each | — | 10 each | 10 each |
| middle layer | resin | — | A | A | A | B | A | A | A | A | A |
| | thickness | μ | 280 | 240 | 200 | 50 | 280 | 280 | — | 280 | 280 |
| sheet thickness | | μ | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| front & back layer/whole layer thickness ratio (μ) | | — | 0.07 | 0.2 | 0.33 | 0.17 | 0.07 | 0.07 | 0 | 0.07 | 0.07 |
| Crystalinity | | % | 9 | 8 | 8 | 7 | 8 | 4 | 8 | 33 | 9 |
| Forming temp. | | ℃ | 100 | 100 | 100 | 100 | 120 | 100 | 100 | 100 | 75 |
| Heat resistance | Volume reduction ratio | % | 1.5 | 1 | 0.5 | 1.1 | 0.8 | 1.1 | 85 | 1 | 31.5 |
| Shock resistance | | kgf·mm | 15 | 25 | 50 | 24 | 14 | 15 | 4 | 17 | 15 |
| Haze | | % | 9 | 26 | 45 | 20 | 30 | 9 | 3 | Unmeasurable | 9 |
| Formability | | — | ○ | ○ | ○ | ○ | ○ | ○ | ○ | × | △ |

◆A: Polylactic acid–family resin B: Biodegradable resin other than polylactic acid–family resin

◆Crystallinity: Crystallinity of polylactic acid–family resin in biodegradable laminate sheet

◆Forming temperature: Temperature of biodegradable laminate sheet during forming

## Claims

1. A biodegradable laminate sheet having a non-stretched polylactic acid-family resin layer of which the crystallinity is 20% or less, and a layer comprising a biodegradable resin other than a polylactic acid-family resin.

2. A biodegradable laminate sheet as claimed in claim 1 wherein said biodegradable resin other than a polylactic acid-family resin is a biodegradable aliphatic polyester other than a polylactic acid-family resin having the glass transition temperature of 0°C or less and the melting point of 80°C or over.

3. A biodegradable laminate sheet as claimed in claim 1 or 2 which is formed of at least three layers, wherein layers comprising said biodegradable resin other than a polylactic acid-family resin form outer layers, and wherein said non-stretched polylactic acid-family resin is at least one layer sandwiched between said outer layers.

4. A biodegradable laminate sheet as claimed in claim 1 or 2 which is formed of at least three layers, wherein said non-stretched polylactic acid-family resin is outer layers, and wherein the layer comprising said biodegradable resin other than a polylactic acid-family resin is at least one layer sandwiched between said outer layers.

5. A biodegradable laminate sheet as claimed in any of claims 1-4 wherein said non-stretched polylactic acid-family resin and the layer comprising the biodegradable resin other than a polylactic acid-family resin are laminted by co-extrusion.

6. A method of forming a biodegradable laminate sheet wherein a biodegradable laminate sheet as claimed in any of claims 1-5 is formed at a temperature not less than the melting point of said biodegradable resin other than a polylactic acid-family resin or more.

7. A formed body using a biodegradable laminate sheet as claimed in any of claims 1-5.



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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP03/08821

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] B32B27/36,

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] B32B1/00-35/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1926-1996 | Toroku Jitsuyo Shinan Koho | 1994-2003 |
| Kokai Jitsuyo Shinan Koho | 1971-2003 | Jitsuyo Shinan Toroku Koho | 1996-2003 |

Electronic data base consulted during the international search (name of data base and, where practicable, 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<br>Y | JP 8-323946 A (Mitsubishi Plastics, Inc.),<br>10 December, 1996 (10.12.96),<br>Claims; Par. Nos. [0067], [0071]; example 7<br>(Family: none) | 1-3,5-7<br>1-3,5-7 |
| X<br>Y | EP 1008629 A (DAICEL CHEMICAL INDUSTRIES, LTD.),<br>14 June, 2000 (14.06.00),<br>Full text<br>& JP 2000-238194 A<br>Full text; particularly, examples 3, 5 | 1,2,4-7<br>1,2,4-7 |
| X | EP 514137 A (MITSUI TOATSU CHEMICALS, INC.),<br>19 November, 1992 (19.11.92),<br>Full text<br>& JP 5-38784 A | 1,6,7 |

☒ Furth er 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
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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
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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 05 September, 2003 (05.09.03) | 24 September, 2003 (24.09.03) |
| Name and mailing address of the ISA/<br>Japanese Patent Office | Authorized officer |
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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP03/08821

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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| Y | JP 7-308961 A (Mitsubishi Plastics, Inc.), 28 November, 1995 (28.11.95), Full text (Family: none) | 1-7 |
| A | JP 10-100353 A (Mitsubishi Plastics, Inc.), 21 April, 1998 (21.04.98), Full text (Family: none) | 1-7 |

Form PCT/ISA/210 (continuation of second sheet) (July 1998)



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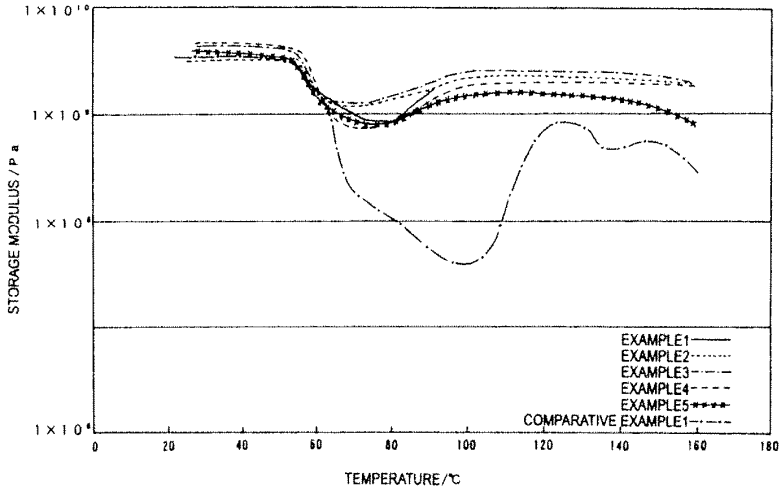
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(54) **Composite composition and molding using the same**

(57) A composite composition includes at least one organic polymer compound having biodegradability, vegetable fibers, and a hydrolysis inhibitor for the organic polymer compound having biodegradability.

FIGURE 1




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## Description

CROSS REFERENCES TO RELATED APPLICATIONS

**[0001]** The present invention contains subject matter related to Japanese Patent Application JP 2004-247010 filed in the Japanese Patent Office on August 26, 2004, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

**[0002]** The present invention relates to a composite composition biodegradable in the natural environment and having heat resistance and use durability sufficient for practical use.

2. Description of the Related Art

**[0003]** In recent years, a wide variety of synthetic resin materials have been developed and provided, and the amounts of these resin materials used in various industrial fields have been increasing year after year. As a result, the amount of synthetic resin waste tends to increase. However, the incineration of synthetic resin waste without any treatment may produce a toxic gas and damage an incinerator due to large combustion heat, thereby causing the large problem of environmental loads.

**[0004]** A known method for treating waste resins includes decreasing the molecular weights of the waste resins by treatment, such as thermal decomposition or chemical decomposition, and then disposing the resins by incineration or landfill.

**[0005]** However, incineration is accompanied with emission of carbon dioxide and thus causes global warming.

**[0006]** When the resin to be incinerated contains sulfur, nitrogen, halogen, or the like, incineration produces a toxic gas and thus brings about air pollution.

**[0007]** On the other hand, when resins are disposed by inappropriate landfill, the resins remain undecomposed for a long period of time because most of resins which are currently used for various purposes are chemically stable, thereby causing soil pollution.

**[0008]** In order to solvent the above-described problem of the environmental effect of synthetic resins, recently, various biodegradable resins have been being developed and brought into practical applications.

**[0009]** The biodegradable resins have the property of being biochemically decomposed into carbon dioxide, water, and the like by microorganisms or the like, and even when the resins are discarded in a natural environment, they are easily degraded into lower-molecular-weight compounds and finally converted to harmless compounds. Therefore, the biodegradable resins are characterized by decreasing the adverse effect of waste disposal on the global environment. For this reason, the practical applications of the biodegradable resins have been particularly advanced to disposable goods such as convenience goods, sanitary goods, and play goods.

**[0010]** As described above, it is said that the biodegradable resins have an excellent effect in view of the preservation of the natural environment. However, from a practical viewpoint, the resins still have many problems to be solved.

**[0011]** For example, materials such as casings of electric appliances and automobile interior materials preferably have heat resistance, but the biodegradable resins have relatively low heat resistance. Therefore, a technique for mixing organic fibers such as cotton fibers, wood fibers, bamboo fibers, or the like with a biodegradable resin has been proposed (refer to, for example, Japanese Unexamined Patent Application Publication Nos. 9-302235, 2000-160034, and 2003-313417).

SUMMARY OF THE INVENTION

**[0012]** In consideration of the fact that biodegradable resins are used for various moldings such as electric appliances and automobile interior materials, which will be more precisely produced by further advanced technology in future, there are demands to further improve rigidity and heat resistance and significantly improve preservation stability

(use durability).

**[0013]** For example, even when a drive source generates heat or a precision actuator locally generates heat, a molding is preferably not thermally deformed. However, when polylactic acid which is a biodegradable resin is applied to an electric machine casing or an automobile interior material on which the drive source or actuator is mounted, there occurs the problem of significantly decreasing storage modulus in a temperature region over the glass transition temperature



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(58°C) of polylactic acid. Therefore, it is desired to significantly improve heat resistance, for solving the problem.

**[0014]** Also, for example, a small audio good preferably maintains the physical properties such as strength at 30°C and a relative humidity of 80% for 5 to 7 hears. However, a sufficient storage property has not been realized by the above-described proposed technique, and thus improvement in durability (durability in a constant temperature and humidity environment) is desired for resolving the problem of sufficient storage property.

**[0015]** Accordingly, the invention provides a composite composition capable of decreasing the influence of disposal on the natural environment and having excellent biodegradability, practically sufficient heat resistance and excellent mechanical strength, and also having sufficient durable, i.e., storage property, even when used for electric appliances and automobile interior materials.

**[0016]** In accordance with an embodiment of the invention, there are provided a composite composition containing at least one organic polymer compound having biodegradability, vegetable fibers, and a hydrolysis inhibitor for the biodegradable organic polymer compound, and a molding produced using the composite composition.

**[0017]** In the invention, mechanical strength and heat resistance are improved by adding the vegetable fibers to the biodegradable resin, and storage durability is improved by adding the hydrolysis inhibitor.

**[0018]** The composite composition is finally biodegraded to harmless substances in a natural environment, thereby effectively decreasing the influence on the environment. Also, when the composite composition is used for a casing of a device including a heat source such as a drive source or a power supply, practically sufficient mechanical strength, heat resistance, and use durability (storage property) may be exhibited.

**[0019]** In other words, the composite composition has a ternary system containing the biodegradable resin, the vegetable fibers, and the hydrolysis inhibitor, and thus has biodegradability, heat resistance, mechanical strength, and storage property.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0020]** Fig. 1 is a graph showing the test results of viscoelasticity of samples of examples and a comparative example.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0021]** An embodiment of the invention will be described in detail below, but the invention is not limited to this embodiment.

**[0022]** In accordance with an embodiment of the invention, a composite composition contains at least one organic polymer compound having biodegradability, vegetable fibers, and a hydrolysis inhibitor.

**[0023]** First, the organic polymer compound having biodegradability will be described.

**[0024]** The organic polymer compound having biodegradability (referred to as the "biodegradable polymer compound" hereinafter) is a compound which is, after use, converted to low-molecular-weight compounds and finally decomposed into water and carbon dioxide by microorganisms in the natural world (Biodegradable Plastic Society, ISO/TC-207/SC3).

**[0025]** The biodegradable polymer compound is preferably a biodegradable resin, for example, a polysaccharide, a peptide, an aliphatic polyester, a polyamino acid, polyvinyl alcohol, a polyamide, polyalkylene glycol, or the like, which has biodegradability, or a copolymer containing at least one of these compounds.

**[0026]** In particular, an aliphatic polyester is excellent in mixing property and mass productivity, and is thus a material suitable for practical application.

**[0027]** The aliphatic polyester is more preferably polylactic acid such as poly-L-lactic acid (PLLA) or a random copolymer of L-lactic acid and D-lactic acid, or a derivative thereof. A general polylactic acid is a crystalline polymer having a melting point of about 160 to 170°C, a glass transition temperature of about 58°C, and excellent biodegradability.

In accordance with an embodiment of the present invention, heat resistance may be improved to a higher temperature, and the storage property suitable for durable consumer goods material may be also secured, as described below.

**[0028]** Other examples of the aliphatic polyester include polycaprolactone, polyhydroxybutyric acid, polyhydroxyvaleric acid, polyethylene succinate, polybutylene succinate, polybutylene adipate, polymalic acid, polyglycolic acid, polysuccinates, polyoxalates, butylene polydiglycolate, polydioxanone, and microbially-synthesized polyesters, e.g., 3-hydroxybutylate (3HB), 3-hydroxyvalerate (3HV), and copolymers thereof.

**[0029]** The molecular weight (number-average molecular weight) of the aliphatic polyester is preferably about 30,000 to 200,000.

**[0030]** With a molecular weight less than 30,000, the strength of the composite composition obtained as a final product becomes insufficient, while with a molecular weight of over 200,000, moldability and formability degrade.

**[0031]** Examples of the polysaccharide include cellulose, starch, chitin, chitosan, and dextran, derivatives thereof, and copolymers containing at least one of these compounds.

**[0032]** Examples of the peptide include collagen, casein, fibrin, and gelatin.

**[0033]** Examples of the polyamide include nylon 4 and nylon 2/nylon 6 copolymers.



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**[0034]** When a polysaccharide is used, any of various plasticizers may be added for imparting thermoplasticity.

**[0035]** Furthermore, an organic polymer compound which exhibits biodegradability with a low molecular weight but exhibits lower biodegradability with a high molecular weight may be used as long as biodegradability is achieved by graft copolymerization with a biodegradable polymer compound. For example, polyethylene, a polyacrylic acid derivative, polypropylene, polyurethane, or the like may be used.

**[0036]** The molecular weights and the terminal groups of these resins are not particularly limited as long as mechanical strength is achieved by polymerization.

**[0037]** The biodegradable polymer compound may be prepared by a know method.

**[0038]** For example, the biodegradable polyester may be prepared by a lactide process, polycondensation of a polyhydric alcohol and a polybasic acid, or intermolecular polycondensation of a hydroxycarboxylic acid having a hydroxyl group and a carboxyl group in its molecule.

**[0039]** Next, description will be made of the vegetable fibers which constitute the composite composition according to an embodiment of the invention.

**[0040]** The vegetable fibers are not particularly limited, but cotton fibers and paper fibers are preferred.

**[0041]** The cotton fibers preferably have an average fiber diameter of 100 μm or less. This is because with an average fiber diameter over 100 μm, dispersibility in the biodegradable polymer compound decreases, and the effect of improving the rigidity and heat resistance of the composite composition obtained as the final target becomes unsatisfactory. The technical lower limit of the average fiber diameter is not particularly limited.

**[0042]** The cotton fibers and paper fibers are preferably used after degreasing for removing a fat component. By removing a fat component from the cotton fibers, the fibers are easily uniformly dispersed in the biodegradable polymer compound, thereby exhibiting the effect of improving the rigidity and heat resistance of the composite composition as the final target and also the effect of suppressing coloring with the cotton fibers. However, when coloring or the like causes no problem with the appearance, degreasing may be not performed.

**[0043]** Furthermore, the cotton fibers and paper fibers are preferably subjected to chemical surface treatment for improving affinity for the biodegradable polymer compound and the dispersibility therein. Examples of the surface treatment include acylation such as acetylation and benzoylation, and silane coupling treatment.

**[0044]** Such surface treatment improves the surface adhesion to the biodegradable polymer compound, for example, an aliphatic polyester, thereby suppressing a decrease in strength due to peeling at the interfaces between the resin and the fibers.

**[0045]** The mixing ratio (weight ratio) of the biodegradable polymer compound (e.g., an aliphatic polyester) to the vegetable fibers is preferably 95/5 to 40/60 (aliphatic polyester/vegetable fibers)

**[0046]** With a vegetable fiber content of less than 5% by weight, the sufficient effect of improving heat resistance is not obtained, while with a vegetable fiber content of over 60% by weight, a problem with a practical material, such as a decrease in strength of the composite composition as the final product, or the like occurs.

**[0047]** As the vegetable fibers, the cotton fibers and the paper fibers are preferred, and chopped hemp or cotton is preferred. The chopped hemp or cotton includes microfibers obtained by colleting fiber dust produced in machine weaving.

**[0048]** Next, the hydrolysis inhibitor constituting the composite composition according to an embodiment of the invention will be described.

**[0049]** The hydrolysis inhibitor is an additive, e.g., a compound having reactivity to active hydrogen of the biodegradable polymer compound, for suppressing hydrolysis of the biodegradable polymer compound. This compound decreases the amount of active hydrogen in the biodegradable polymer compound and avoids catalytic hydrolysis of the biodegradable polymer chain with the active hydrogen.

**[0050]** The active hydrogen means hydrogen in a bond (N-H bond or O-H bond) between hydrogen and oxygen, nitrogen, or the like, and such hydrogen has higher reactivity than that of hydrogen in a carbon-hydrogen bond (C-H bond). Specifically, the active hydrogen is hydrogen of, for example, a carboxyl group (-COOH), a hydroxyl group (-OH), an amino group ($-NH_2$), or an amide bond (-NHCO-), in the biodegradable polymer compound.

**[0051]** Examples of the compound having reactivity to the active hydrogen in the biodegradable polymer compound include carbodiimide compounds, isocyanate compounds, and oxozoline compounds. In particular, the carbodiimide compounds are melt-kneadable with the biodegradable polymer compound and thus exhibit the effect of suppressing hydrolyzability of the polymer compound in a small adding amount.

**[0052]** The carbodiimide compounds have at least one carbodiimide group per molecule and include polycarbodiimide compounds.

**[0053]** A carbodiimide compound is synthesized by, for example, a method of decarboxylation polycondensation of any one of various polymer isocyanates at about 70°C or more in an inert solvent (e.g., hexane, benzene, dioxane, or chloroform) or without a solvent using, as a catalyst, an organophosphorus compound such as O,O-dimethyl-O-(3-methyl-4-nitrophenyl) phosphorothioate, O,O-dimethyl-O-(3-methyl-4-(methylthio)phenyl) phosphorothioate, or O,O-diethyl-O-2-isopropyl-6-methylpyrimidine-4-yl phosphorothioate (O represents any number), or an organometallic compound such as a rhodium complex, a titanium complex, a tungsten complex, or a palladium complex.



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**[0054]** Examples of a monocarbodiimide compound which is one of the carbodiimide compounds include dicyclohexylcarbodiimide, diisopropylcarbodiimide, dimethylcarbodiimide, diisobutylcarbodiimide, dioctylcarbodiimide, diphenylcarbodiimide, and naphthylcarbodiimide. In particular, dicyclohexylcarbodiimide and diisopropylcarbodiimide are preferred because they are industrially easily available.

**[0055]** Examples of the isocyanate compounds include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 2,2'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, 1,5-tetrahydronaphthalene diisocyanate, tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, trimethylhexamethylene diisocyanate, 1,3-cyclohexylene diisocyanate, 1,4-cyclohexylene diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, hydrogenated xylylene diisocyanate, lysine diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, and 3,3'-dimethyl-4,4'-dicyclohexylmethane diisocyanate.

**[0056]** The isocyanate compounds may be synthesized by a known method, and commercially-available isocyanate compounds may be appropriately used.

**[0057]** Applicable examples of commercially available polyisocyanate compounds include aromatic isocyanate adducts, such as Coronate (trade named, manufactured by Nippon Polyurethane Industries Co., Ltd., hydrogenated diphenylmethane diisocyanate) and Millionate (trade named, manufactured by Nippon Polyurethane Industries Co., Ltd.).

**[0058]** In particular, a solid polyisocyanate compound in which for example, an isocyanate group is blocked with a masking agent (a polyhydric aliphatic alcohol, an aromatic polyol, or the like) is more preferred than a liquid.

**[0059]** Examples of the oxazoline compounds include 2,2'-o-phenylenebis(2-oxazoline), 2,2'-m-phenylenebis(2-oxazoline), 2,2'-p-phenylenebis(2-oxazoline), 2,2'-p-phenylenebis(4-methyl-2-oxazoline), 2,2'-m-phenylenebis(4-methyl-2-oxazoline), 2,2'-p-phenylenebis(4,4'-dimethyl-2-oxazoline), 2,2'-m-phenylenebis(4,4'-dimethyl-2-oxazoline), 2,2'-ethylenebis(2-oxazoline), 2,2'-tetramethylenebis(2-oxazoline), 2,2'-hexamethylenebis(2-oxazoline), 2,2'-octamethylenebis(2-oxazoline), 2,2'-ethylenebis(4-methyl-2-oxazoline), and 2,2'-diphenylenebis(2-oxazoline).

**[0060]** The biodegradation speed and mechanical strength of the composite composition obtained as the final product may be controlled by controlling the type and adding amount of the hydrolysis inhibitor. Therefore, the type and mixing amount of the hydrolysis inhibitor are determined according to the type of the molding produced using the composite composition according to an embodiment of the invention.

**[0061]** Specifically, the amount of the hydrolysis inhibitor added is preferably about 7% by weight or less.

**[0062]** As the hydrolysis inhibitor, the compounds listed above may be used alone or in combination of two or more.

**[0063]** The method for producing the composite composition according to an embodiment of the invention is not particularly limited, and a know method may be used.

**[0064]** For example, the composite composition may be produced by melt-kneading the biodegradable polymer compound with the vegetable fibers and the hydrolysis inhibitor.

**[0065]** Specifically, the vegetable fibers and the hydrolysis inhibitor are added and mixed in a pre-step or melting step of melting the biodegradable organic polymer compound.

**[0066]** The vegetable fibers and the hydrolysis inhibitor may be added simultaneously or separately. When both are added separately, they may be added in any desired order.

**[0067]** Also, one of the vegetable fibers and the hydrolysis inhibitor may be added and mixed after the biodegradable organic polymer compound is melted, the resulting composite composition may be again melted, and then the other of the hydrolysis inhibitor and the vegetable fibers may be added and mixed.

**[0068]** The composite composition according to an embodiment of the invention may contain various additives such as a flame retardant, a lubricant, a wax, a plasticizer, a thermal stabilizer, a reinforcing agent, an inorganic or organic filler, a colorant, an antioxidant, an ultraviolet absorber, and a crystallization promoter.

**[0069]** The content of each of the additives is preferably 0.1% by weight or less and less than 50% by weight. With a content of less than 0.1% by weight, each of the functions is difficult to exhibit, while with a content over 50% by weight, the target physical properties (biodegradability, heat resistance, and preservation stability) of the composite composition according to an embodiment of the invention may be inhibited.

**[0070]** Examples of the flame retardant include various boric acid flame-retardant compounds, phosphorus flame-retardant compounds, inorganic flame-retardant compounds, nitrogen flame-retardant compounds, halogen flame-retardant compounds, organic flame-retardant compounds, and colloidal flame-retardant compounds. Specific materials are given below, but these materials may be used alone or as a mixture of two or more.

**[0071]** Examples of the boric acid flame-retardant compounds include zinc borate hydrate, barium metaborate, and borax.

**[0072]** Examples of the phosphorus flame-retardant compounds include ammonium phosphate, ammonium polyphosphate, melamine phosphate, red phosphorus, phosphoric acid esters, tris(chloroethyl) phosphate, tris(monochloropropyl) phosphate, tris(dichloropropyl) phosphate, triallyl phosphate, tris(3-hydroxypropyl) phosphate, tris(tribromophenyl) phosphate, tris-β-chloropropyl phosphate, tris(dibromophenyl) phosphate, tris(tribromoneopentyl) phosphate, tetrakis(2-chlo-



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roethyl)ethylene diphosphate, dimethylmethyl phosphate, tris(2-chloroethyl) orthophosphate, aromatic condensed phosphates, halogen-containing condensed organic phosphates, ethylene-bis-tris(2-cyanoethyl)phosphonium bromide, ammonium polyphosphate, β-chloroethyl acid phosphates, butyl pyrophosphate, butyl acid phosphate, butoxyethyl acid phosphate, 2-ethylhexyl acid phosphate, melamine phosphate, halogen-containing phosphates, and phenylphosphonic acid.

**[0073]** Examples of the inorganic flame-retardant compounds include metal sulfate compounds, such as zinc sulfate, potassium hydrogen sulfate, aluminum sulfate, antimony sulfate, sulfuric acid esters, potassium sulfate, cobalt sulfate, sodium hydrogen sulfate, iron sulfate, copper sulfate, sodium sulfate, nickel sulfate, barium sulfate, and magnesium sulfate; ammonium flame-retardant compounds such as ammonium sulfate; iron oxide combustion catalysts such as ferrocene; metal nitrate compounds such as copper nitrate; titanium-containing compounds such as titanium oxide; guanidine compounds such as guanidine sulfamate; and other compounds such as zirconium compounds, molybdenum compounds, tin compounds, carbonate compounds such as potassium carbonate, aluminum hydroxide, metal hydroxides such as magnesium hydroxide, and modified products thereof.

**[0074]** Examples of the nitrogen flame-retardant compounds include cyanurate compounds having triazine rings.

**[0075]** Examples of the halogen flame-retardant compounds include halogen-containing flame-retardant compounds, such as chlorinated paraffins, perchlorocyclopentadecane, hexabromobenzene, decabromodiphenyl oxide, bis(tribromophenoxy)ethane, ethylenebis-dibromonorbornane dicarboxyimide, ethylenebis-tetrabromophthalimide, dibromoethyl-dibromocyclohexane, dibromoneopentyl glycol, 2,4,6-tribromophenol, tribromophenyl allyl ether, tetrabromobisphenol A derivatives, tetrabromobisphenol S derivatives, tetradecabromo-diphenoxybenzene, tris-(2,3-dibromopropyl)-isocyanurate, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxyethoxy-3,5-dibromophenyl)propane, poly (pentabromobenzylacrylate), tribromostyrene, tribromophenylmaleimide, tribromoneopentyl alcohol, tetrabromodipentaerythritol, pentabromobenzyl acrylate, pentabromophenol, pentabromotoluene, pentabromodiphenyl oxide, hexabromocyclododecane, hexabromodiphenyl ether, octabromophenol ether, octadibromodiphenyl ether, octabromodiphenyl oxide, magnesium hydroxide, dibromoneopentyl glycol tetracarbonate, bis(tribromophenyl)fumaramide, N-methylhexabromodiphenylamine, styrene bromide, and diallyl chlorendate.

**[0076]** Examples of the organic flame-retardant compounds include chlorendic anhydride, phthalic anhydride, bisphenol A-containing compounds, glycidyl compounds such as glycidyl ether, polyhydric alcohols such as ethylene glycol and pentaerythritol, modified carbamide, silicone oil, and silica compounds such as silicon dioxide, low-melting-point glass, and organosiloxanes.

**[0077]** Examples of the colloidal flame-retardant compounds include colloids of flame-retardant compounds, such as known usual hydroxides having flame retardancy, e.g., aluminum hydroxide, magnesium hydroxide, and calcium hydroxide; hydrates, e.g., calcium aluminate, calcium sulfate dihydrate, zinc borate, barium metaborate, borax, and kaoline clay; nitric acid compounds, e.g., sodium nitrate; molybdenum compounds; zirconium compounds; antimony compounds; dawsonite; and plogopite.

**[0078]** A flame-retardant additive preferably applies no load on the environment in disposal, for example, generation of a harmful gas in incineration.

**[0079]** From the viewpoint of this environment friendliness, preferred examples of the flame-retardant additive include hydroxide compounds such as aluminum hydroxide, magnesium hydroxide, and calcium hydroxide; the above-described phosphorus compound, particularly ammonium phosphate compounds such as ammonium phosphate and ammonium polyphosphate; and silica compounds such as silicon dioxide, low-melting-point glass, and organosiloxanes.

**[0080]** A silica compound used as the flame-retardant additive preferably contains 50% or more of silicon dioxide. Since a silica compound is collected from a natural mineral, the silica compound contains other substances, e.g., MgO, CaO, $Fe_2O_3$, $Al_2O_3$, and the like, to some extent. However, it is desirable that the flame-retardant effect is not inhibited by impurities.

**[0081]** A hydroxide compound used as the flame-retardant additive preferably has a purity of about 99.5% or more because the higher the purity, the more the preservation stability is improved by combination with the hydrolysis inhibitor described below.

**[0082]** The purity of the hydroxide compound may be measured by a known method. For example, the content of the impurities in the hydroxide compound is measured by a known method, and the content of impurities is subtracted from the total amount to determine the purity of the hydroxide compound. More specifically, for example, aluminum hydroxide contains impurities such as $Fe_2O_3$, $SiO_2$, T-$Na_2O$, and S-$Na_2O$. The content of $Fe_2O_3$ is determined by O-phenanthroline spectrophotometry (JIS H 1901) after the compound is dissolved in a sodium carbonate-boric acid solution. The content of $SiO_2$ is determined by molybdenum blue spectrophotometry (JIS H 1901) after the compound is dissolved in a sodium carbonate-boric acid solution. The content of T-$Na_2O$ is determined by flame photometry after the compound is dissolved in sulfuric acid, and the content of S-$Na_2O$ is determined by flame photometry after the compound is extracted with hot water. The thus-determined contents are subtracted from the weight of aluminum hydroxide to determine the purity of the hydroxide. With a purity of 99.5% or more, of course, plural types of flame-retardant hydroxide compounds may be combined.



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**[0083]** The shape of the flame-retardant additive is not particularly limited, but a granular shape is preferred. The grain size is appropriately selected according to the type used.

**[0084]** For example, when the flame-retardant additive is the silica compound such as $SiO_2$ or glass, the average grain size determined by laser diffraction is preferably about 50 μm or less. In this case, the grain size distribution is not particularly limited.

**[0085]** When the flame-retardant additive is a hydroxide compound such as $Al(OH)_3$, $Mg(OH)_2$, or $Ca(OH)_2$, the average grain size determined by laser diffraction is preferably about 100 μm or less. In this case, the grain size distribution is not particularly limited.

**[0086]** In view of dispersibility in kneading and injection moldability in a molding process for forming a molding using the composite composition according to an embodiment of the invention, the average grain size of the flame-retardant additive is preferably in the above range. Within the range, a smaller value is more preferred.

**[0087]** In order to improve the filling rate in the composition, plural types of flame-retardant additives having different average grain sizes may be combined.

**[0088]** Furthermore, when the flame-retardant additive is a hydroxide compound such as $Al(OH)_3$, $Mg(OH)_2$, or Ca $(OH)_2$, grains preferably have a BET specific surface area of about 5.0 $m^2/g$ or less determined by a nitrogen gas adsorption method.

**[0089]** In order to improve the filling rate in the composition, plural types of flame-retardant additives having different BET specific surface areas may be combined.

**[0090]** In view of moldability, the BET specific surface area is preferably about 5.0 $m^2/g$ or less, and a lower value is more preferred.

**[0091]** The amount of the flame-retardant additive added is appropriately determined in a range in which the mechanical strength of the composite composition according to an embodiment of the invention may be secured.

**[0092]** Specifically, when the flame-retardant additive is a hydroxide compound such as $Al(OH)_3$, $Mg(OH)_2$, or Ca $(OH)_2$, the amount of the flame-retardant additive added is about 5 to 50% by weight, preferably about 7.5 to 45% by weight, and more preferably about 10 to 40% by weight.

**[0093]** When the flame-retardant additive is an ammonium (poly) phosphate compound such as $(NH_4)_3(PhO_{3n+1})_{n+2}$ (n is a natural number), the amount of the flame-retardant additive added is about 1 to 25% by weight, preferably about 2 to 20% by weight, and more preferably about 3 to 15% by weight.

**[0094]** When the flame-retardant additive is a silica compound such as $SiO_2$ or glass, the amount of the flame-retardant additive added is about 5 to 40% by weight, preferably about 10 to 35% by weight, and more preferably about 15 to 30% by weight.

**[0095]** Examples of the reinforcing material include glass microbeads, carbon fibers, chalk, quartz such as novoculite, asbestos, and silicates such as feldspar, mica, talc, wollastonite, and kaoline.

**[0096]** Examples of the inorganic filler include fine particles of carbon; silicon dioxide; metal oxides such as alumina, silica, magnesia, and ferrite; silicates such as talc, mica, kaoline, and zeolite; barium sulfate; calcium carbonate; silicon nitride; silicides such as carbon silicide; and fullerene.

**[0097]** Examples of the organic filler include epoxy resins, melamine resins, urea resins, acrylic resins, phenol resins, polyimide resins, polyamide resins, polyester resins, and Teflon (trade name) resin.

**[0098]** In particular, silicon dioxide and silicides are preferred. The above-described fillers may be used alone or as a mixture of two or more.

**[0099]** Examples of the antioxidant include phenolic, amine, phosphoric, sulfuric, hydroquinone, and quinoline antioxidants.

**[0100]** Examples of the phenolic antioxidants include hindered phenols, such as 2,6-di-tert-butyl-p-cresol, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 2,2'-methylenebis(4-methyl-6-tertbutylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), and $C_{2-10}$ alkylenediol-bis [3-(3,5-di-branched $C_{3-6}$ alkyl-4-hydroxyphenyl) propionate], e.g., 1,6-hexanediolbis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]; di- or tri-oxy $C_{2-4}$ alkylenediol-bis[3-(3,5-di-branched $C_{3-6}$ alkyl-4-hydroxyphenyl)propionate], e.g., triethyleneglycol-bis[3-(3-tert-butyl-5-metyl-4-hydroxyphenyl)propionate]; $C_{3-8}$ alkanetriol-bis[3-(3,5-di-branched $C_{3-6}$ alkyl-4-hydroxyphenyl]propionate], e.g., glycerin tris[3-(3,5-di-tert-butyl-4-hydoxyphenyl)propionate]; $C_{4-8}$ alkane tetraol tetrakis [3- (3, 5-di-branched $C_{3-6}$ alkyl-4-hydroxyphenyl)propionate], e.g., pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxypheny)propionate]; n-octadecyl-3-(4',5'-di-tert-butylphenol)propionate, n-octadecyl-3-(4'-hydoxy-3', 5'-di-tert-butylphenol)propionate, stearyl-2-(3,5-di-tert-butyl-4-hydroxyphenol)propionate, distearyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 2-tert-butyl-6-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenyl acrylate, N.N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamide), 3,9-bis{2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]-1,1-dimethylethyl}-2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-tertbutylphenol), and 1,1,3-tris(2-methyl-4-hydroxy-5-tertbutylphenol)butane.

**[0101]** Examples of the amine antioxidants include phenyl-1-naphthylamine, phenyl-2-naphthylamine, N,N'-diphenyl-1,4-phenylenediamine, and N-phenyl-N'-cyclohexyl-1,4-phenylenediamine.



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**[0102]** Examples of the phosphoric antioxidants include phosphite compounds, such as triisodecyl phosphite, triphenyl phosphite, trisnonylphenyl phosphite, diphenylisodecyl phosphite, phenyldiisodecyl phosphite, 2,2-methylenebis (4,6-di-tert-butylphenyl)octyl phosphite, 4,4'-butylidenebis(3-methyl-6-tert-butylphenyl)ditridecyl phosphite, tris (2,4-di-tert-butylphenyl) phosphite, tris(2-tert-butyl-4-methylphenyl) phosphite, tris(2,4-di-tert-amylphenyl) phosphite, tris (2-tert-butylphenyl) phosphite, bis(2-tert-butylphenyl)phenyl phosphite, tris[2-(1,1-dimethylpropyl)-phenyl] phosphite, tris [2,4-(1,1-dimethylpropyl)phenyl] phosphite, tris(2-cyclohexylphenyl) phosphite, and tris(2-tert-butyl-4-phenylphenyl) phosphite; and phosphine compounds, such as triethylphosphine, tripropylphophine, tributylphosphine, tricyclohexylphosphine, diphenylvinylphosphine, allyldiphenylphosphine, triphenylphosphine, methylphenyl-p-anisylphosphine, p-anisyldiphenylphosphine, p-tolyldiphenylphosphine, di-p-anisylphenylphosphine, di-p-tolylphenylphosphine, tri-m-aminophenylphosphine, tri-2,4-dimethylphenylphosphine, tri-2,4,6-trimethylphenylphosphine, tri-o-tolylphosphine, tri-m-tolylphosphine, tri-p-tolylphosphine, tri-o-anisylphosphine, tri-p-anisylphosphine, and 1,4-bis(diphenylphosphino)butane.

**[0103]** Examples of the hydroquinone antioxidants include 2,5-di-tert-butylhydroquinone.

**[0104]** Examples of the quinoline antioxidants include 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.

**[0105]** Examples of the sulfuric antioxidants include dilauryl thiodipropionate and distearyl thiodipropionate.

**[0106]** Among these antioxidants, the phenolic antioxidants (particularly, hindered phenols), e.g., polyolpoly[(branched $C_{3-6}$ alkyl group and hydroxyl group-substituted phenyl)propionate], are particularly preferred.

**[0107]** The above-described antioxidants may be used alone or in combination or two or more.

**[0108]** Examples of the thermal stabilizer include nitrogen-containing compounds such as basic nitrogen-containing compounds, e.g., polyamide, poly-β-alanine copolymers, polyacrylamide, polyurethane, melamine, cyanoguanidine, and melamine-formaldehyde condensates; alkali or alkaline earth metal-containing compounds, such as organic carboxylic acid metal salts (e.g., calcium stearate and calcium 12-hydroxystearate), metal oxides (e.g., magnesium oxide, calcium oxide, and aluminum oxide), metal hydroxides (e.g., magnesium hydroxide, calcium hydroxide, and aluminum hydroxide), and metal carbonates; zeolite, and hydrotalcite.

**[0109]** In particular, the alkali or alkaline earth metal-containing compounds (particularly, alkaline earth metal-containing compounds, such as magnesium compounds and calcium compounds), zeolite, and hydrotalcite are preferred.

**[0110]** The these thermal stabilizers may be used alone or in combination of two or more.

**[0111]** Examples of the ultraviolet absorber includes those of a known benzophenone type, benzotriazole type, cyanoacrylate type, salicylate type, and anilide oxalate type.

**[0112]** Specific examples of the ultraviolet absorber include [2-hydroxy-4-(methacryloyloxyethoxy)benzophenone] -methyl methacrylate copolymer, [2-hydroxy-4-(methacryloyloxymethoxy)benzophenone]-methyl methacrylate copolymer, [2-hydroxy-4-(methacryloyloxyoctoxy)benzophenone]-methyl methacrylate copolymer, [2-hydroxy-4-methacryloyloxydodecyloxy)benzophenone]-methyl methacrylate copolymer, [2-hydroxy-4-(methacryloyloxybenziloxy)benzophenone]-methyl methacrylate copolymer, [2,2'-dihydroxy-4-(methacryloyloxyethoxy)benzophenone]-methyl methacrylate copolymer, [2,2'-dihydroxy-4-(methacryloyloxymethoxy)benzophenone]-methyl methacrylate copolymer, and [2,2'-dihydroxy-4-(methacryloyloxyoctoxy)benzophenone]-methyl methacrylate copolymer.

**[0113]** These ultraviolet absorbers may be used alone or in combination of two or more.

**[0114]** Examples of the lubricant include petroleum lubricants such as liquid paraffin; synthetic lubricants such as halogenated hydrocarbons, diester oil, silicone oil, and fluorosilicone; various modified silicon oils (epoxy-modified, amino-modified, alkyl-modified, and polyether modified); silicone-based lubricating materials such as copolymers of an organic compound such as polyoxyalkylene glycol and silicone; silicones copolymers; various fluorine surfactants such as fluoroalkyl compounds; fluorine lubricating materials such as trifluoromethylene chloride low-grade polymers; waxes such as paraffin wax and polyethylene wax; higher aliphatic alcohols; higher aliphatic amides; higher fatty acid esters; higher fatty acid salts; and molybdenum disulfide.

**[0115]** In particular, silicone copolymers (prepared by block or graft polymerization of silicone with resin) are preferred.

**[0116]** These silicon copolymers may be prepared by block or graft polymerization of silicon with resin, such as acrylic resin, polystyrene resin, polynitrile resin, polyamide resin, polyolefin resin, epoxy resin, polybutyral resin, melamine resin, vinyl chloride resin, polyurethane resin, or polyvinyl ether resin. In particular, a silicone graft copolymer is preferably used.

**[0117]** The above-described lubricants may be used alone or in combination of two or more.

**[0118]** Examples of the waxes include olefin waxes such as polypropylene wax and polyethylene wax; paraffin waxes; Fischer-Tropsch wax; microcrystalline waxes, montan waxes, fatty acid amide waxes; higher aliphatic alcohol waxes; higher fatty acid waxes; fatty acid ester waxes; carnauba waxes; and rice waxes.

**[0119]** These waxes may be used alone or in combination of two or more.

**[0120]** Examples of the colorant include inorganic pigments, organic pigments, and dyes.

**[0121]** Examples of the inorganic pigments include chromium pigments, cadmium pigments, iron pigments, cobalt pigments, ultramarine, and Prussian blue.

**[0122]** Examples of the organic pigments and dyes include carbon black; phthalocyanine pigments such as copper



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phthalocyanine; quinacridone pigments such as quinacridone magenta and quinacridone red; azo pigments such as hansa yellow, disazo yellow, permanent yellow, permanent red, and naphthol red; nigrosine dyes such as spirit black SB, nigrosine base, and oil black BW; oil blue; pigment yellow; pigment blue; pigment red; and alkali blue.

**[0123]** These colorants may be used alone or in combination of two or more.

**[0124]** Examples of the crystallization promoter include organic acid salts such as sodium p-tert-butylbenzoate, sodium montanate, calcium montanate, sodium palmitate, and calcium stearate; inorganic salts such as calcium carbonate, calcium silicate, magnesium silicate, calcium sulfate, barium sulfate, and talc; and metal oxides such as zinc oxide, magnesium oxide, and titanium oxide.

**[0125]** These crystallization promoters may be used alone or in combination of two or more.

**[0126]** The composite composition according to an embodiment of the invention may be subjected to various known treatments.

**[0127]** For example, in order to suppress hydrolysis of the biodegradable polymer compound, the composite composition may be irradiated with active energy rays. In this case, as the active energy rays, for example, electromagnetic waves, electron beams, or particle rays, or a combination thereof may be used.

**[0128]** Examples of the electromagnetic waves include ultraviolet (UV) rays and X-rays. Examples of the particle rays include rays of element particles such as proton and neutron. In particular, electron beam irradiation using an electron accelerator is preferably performed.

**[0129]** The active energy rays are preferably applied using a known apparatus, for example, a UV irradiation apparatus, an electron accelerator, or the like. The irradiation dose and irradiation strength are not particularly limited as long as hydrolysis of the biodegradable polymer compound in the composite composition is effectively delayed. For example, in use of electron rays, the acceleration voltage is preferably about 100 to 5000 kV, and the irradiation dose is preferably about 1 kGy or more.

**[0130]** The composite composition according to an embodiment of the invention may be use for various applications.

**[0131]** For example, the composite composition may be applied to various moldings such as casings of electric appliances, e.g., a DVD (digital video disk) player, a CD (compact disk) player, a desktop AV apparatus such as an amplifier, a speaker, a vehicle AV/IT apparatus, a cellular phone terminal, a PDA such as an electronic book, a video deck, a television, a projector, a television receiver, a digital video camera, a digital still camera, a printer, a radio, a radio-cassette player, a system stereo, a microphone, a headphone, TV, a keyboard, a portable audio apparatus such as a headphone stereo, a personal computer, and a personal computer peripheral device.

**[0132]** Besides the casings of electric appliances, the composite composition may be also used for applications, such as constituent parts of electric appliances, packing materials, and automobile interior materials.

**[0133]** As a method for producing a molding using the composite composition according to an embodiment of the invention, for example, pressure molding, film molding, extrusion molding, or injection molding is used. In particular, injection molding is preferred.

**[0134]** More specifically, the extrusion molding may be performed using a known extruder, for example, a single-screw extruder, a multi-screw extruder, or a tandem extruder, according to an ordinary method.

**[0135]** The injection molding may be performed using a known injection molding machine, for example, an inline screw injection molding machine, a multilayer injection molding machine, or a double-headed injection molding machine, according to an ordinary method.

Examples

**[0136]** Molding samples were formed using composite compositions according to an embodiment of the invention, and the characteristics thereof were evaluated.

**[0137]** It is to be understood that the present invention is not limited to the examples below.

Examples 1 to 5 and Comparative Examples 1 to 3

Preparation of sample

**[0138]**

(A) Biodegradable resin: polylactic acid (LACEA (H100J, manufactured by Mitsui Chemicals Inc.))
(B) Vegetable fibers
(C) Hydrolysis inhibitor

**[0139]** The above components (A) to (C) were mixed in the amounts shown in Table 1 by a melt kneading method.

**[0140]** Furthermore, predetermined additives were added, and the resultant mixture was kneaded using a Minimax



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Mixtruder (manufactured by Toyo Seiki Co., Ltd.) as a kneader at a nozzle temperature of 170 to 175°C with a torque of 4 to 6 kg and a retention time of 3 seconds or less.

**[0141]** Each of the composite compositions obtained by the above-described process was ground and then pressed at 170°C and 300 kg/cm$^2$ to prepare a plate-shaped molding having a thickness of 1.0 mm.

Table 1 Sample Composition (composition unit: % by weight)

| | Biodegradable resin | Vegetable fiber | Hydrolysis inhibitor |
|---|---|---|---|
| Example 1 | Polylactic acid: 88 | Chopped hemp or cotton: 10 | Dicyclohexylcarbodiimide: 2 |
| Example 2 | Polylactic acid: 83 | Chopped hemp or cotton: 15 | Dicyclohexylcarbodiimide: 2 |
| Example 3 | Polylactic acid: 78 | Chopped hemp or cotton: 20 | Dicyclohexylcarbodiimide: 2 |
| Example 4 | Polylactic acid: 73 | Chopped hemp or cotton: 25 | Dicyclohexylcarbodiimide: 2 |
| Example 5 | Polylactic acid: 93 | Paper fibers: 5 | Dicyclohexylcarbodiimide: 2 |
| Comparative Example 1 | Polylactic acid: 98 | - | Dicyclohexylcarbodiimide: 2 |
| Comparative Example 2 | Polylactic acid: 85 | Chopped hemp or cotton: 15 | - |
| Comparative Example 3 | Polylactic acid: 95 | Paper fibers: 5 | - |

**[0142]** The moldings of the composite compositions prepared as described above were tested with respect to heat resistance (viscoelasticity test under high-temperature conditions) and storage property, as described below.

(Viscoelasticity test)

**[0143]** Measuring apparatus: Viscoelasticity analyzer manufactured by Rheometric Co.,

**[0144]** Sample piece: Composite composition (length 50 mm x width 7 mm x thickness 1 mm) having the composition shown in Table 1

Frequency: 6.28 (rad/s)
Measurement start temperature: 0°C
Measurement final temperature: 160°C
Heating rate: 5 °C/min
Distortion: 0.05%

(Preservation test)

**[0145]** The storage property was evaluated by measuring a change in molecular weight of each of the prepared composite compositions.

**[0146]** The molecular weight of each sample was considered as the initial molecular weight. Each sample was preserved in a constant temperature and humidity bath at 80°C and a relative humidity of 80% for 100 hours and then measured with respect to the molecular weight after preservation.

**[0147]** The molecular weight maintenance ratio of each sample was calculated by dividing the molecular weight after preservation by the initial molecular weight. When the molecular weight maintenance ratio was over 90%, the practical storage property was regarded as "good", and when the molecular weight maintenance ratio was 90% or less, the practical storage property was regarded as "bad". The results are shown in Table 2.

**[0148]** The molecular weigh was measured as follows:

**[0149]** The molecular weight was the weight-average molecular weight (in terms of polystyrene) measured by gel permeation chromatography (GPC).

Apparatus: WILLIPORE Waters 600E system controller
Detector: UV (Waters 484) and RI (Waters 410)
Standard sample: polystyrene
Operation: A sample was dissolved in chloroform so that the concentration was 0.15% by weight, and then stirred for 2 hours to produce a solution, and then the resulting solution was passed through a 0.25 μm filter to prepare a measurement sample for the apparatus.



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[Evaluation of heat resistance]

**[0150]** Fig. 1 shows the results of the viscoelasticity test of the sample of each of Examples 1 to 5 and Comparative Example 1, and the evaluation results are shown in Table 2.

**[0151]** As shown in Fig. 1, the samples of Examples 1 to 5 prepared using the composite compositions according to an embodiment of the invention maintain excellent strength even in a temperature range higher than the glass transition temperature (about 58°C) of the biodegradable resin (polylactic acid), and thus the excellent effect of improving heat resistance is achieved, as compared with the sample of Comparative Example 1 not containing the vegetable fibers.

[Evaluation of storage property]

**[0152]** Table 2 shows the evaluation results of the storage property of the sample of each of Examples 1 to 5 and Comparative Examples 1 to 3.

Table 2

| | Heat resistance | Storage property |
|---|---|---|
| Example 1 | good | good |
| Example 2 | good | good |
| Example 3 | good | good |
| Example 4 | good | good |
| Example 5 | good | good |
| Comparative Example 1 | bad | good |
| Comparative Example 2 | good | bad |
| Comparative Example 1 | good | bad |

**[0153]** As shown in Table 2, with the samples of Examples 1 to 5 according to an embodiment of the invention, the very excellent storage property in a constant temperature and humidity environment was realized by adding the hydrolysis inhibitor.

**[0154]** The above-described results indicate that a composite composition according to an embodiment of the invention contains an organic polymer compound having biodegradability, vegetable fibers, and a hydrolysis inhibitor, and thus has both heat resistance and storage property, thereby realizing practically sufficient storage stability even when used for, for example, a casing for an electronic device or the like in which a power supply or driving source generates heat.

**[0155]** Namely, the composite composition has high heat resistance and stability and may be used for various practical moldings. Also, when disposed, the composite composition is finally decomposed into components safe for living organisms and the global environment, for example, water, carbon dioxide, and the like. Therefore, the composite composition is a material having the minimum influence on environments, and may decrease environmental pollution due to disposal when used for moldings such as casings of various electric appliances and packing materials.

**[0156]** It should be understood by those skilled in the art that various modifications, combinations, sub-combinations and alterations may occur depending on design requirements and other factors insofar as they are within the scope of the appended claims or the equivalents thereof.

## Claims

1. A composite composition comprising:

   at least one organic polymer compound having biodegradability;
   vegetable fibers; and
   a hydrolysis inhibitor for the organic polymer compound having biodegradability.

2. The composite composition according to Claim 1, wherein the organic polymer compound having biodegradability is at least one of a polysaccharide, an aliphatic polyester, a polyamino acid, polyvinyl alcohol, and a polyalkylene glycol, or a copolymer containing at least any of these compounds.



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3. The composite composition according to claim 2, wherein the aliphatic polyester is at least one of polylactic acid, polycaprolactone, polyhydroxybutyric acid, polyhydroxyvaleric acid, polyethylene succinate, polybutylene succinate, polybutylene adipate, polymalic acid, and microbially-synthesized polyesters, or a copolymer containing at least any of these compounds.

4. The composite composition according to claim 1, wherein the vegetable fibers are cotton fibers or paper fibers.

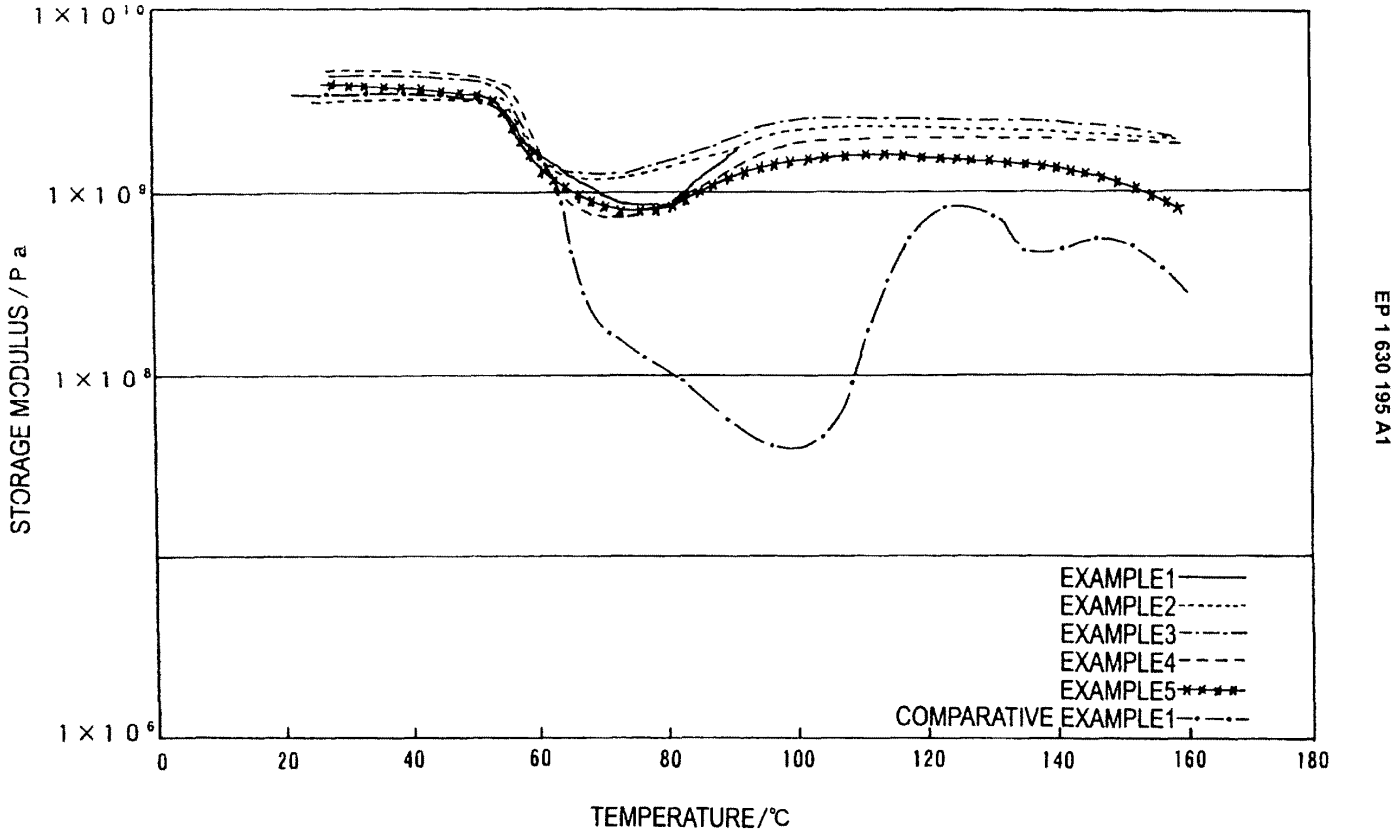
5. The composite composition according to claim 1, wherein the hydrolysis inhibitor is at least one compound of carbodiimide compounds, isocyanate compounds, and oxozoline compounds.

6. A molding produced using a composite composition containing at least one organic polymer compound having biodegradability, vegetable fibers, and a hydrolysis inhibitor for the organic polymer compound having biodegradability.



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FIGURE 1


1×10^10
1×10^9
1×10^8
1×10^6
STORAGE MODULUS / Pa
0
20
40
60
80
100
120
140
160
180
TEMPERATURE/℃
EXAMPLE1
EXAMPLE2
EXAMPLE3
EXAMPLE4
EXAMPLE5
COMPARATIVE EXAMPLE1

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 05 01 7789

## 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) |
|---|---|---|---|
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 1998, no. 08,<br>30 June 1998 (1998-06-30)<br>& JP 10 077395 A (SEKISUI CHEM CO LTD),<br>24 March 1998 (1998-03-24)<br>* abstract *<br>----- | 1-6 | C08K5/00<br>C08L67/04<br>C08K7/02<br>C08K9/00<br>C08K13/00<br>C08J5/18<br>C08J5/04 |
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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 |
|---|---|---|
| Munich | 21 October 2005 | Kiebooms, R |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 01 7789

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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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



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最終頁に続く

(54)【発明の名称】植物繊維樹脂複合成形品の製造方法及び植物繊維樹脂複合成形品

(57)【要約】
【課題】　使用時の耐熱性及び機械的特性に優れ、さらに環境負荷を軽減した植物繊維樹脂複合成形品及び植物繊維樹脂複合成形品の製造方法を提供する。
【解決手段】　植物から得られるリグノセルロース繊維と結晶性の樹脂組成物とを含む植物繊維樹脂複合組成物を、結晶性の樹脂組成物の結晶化温度を基準とした上下３０℃の範囲の温度の金型で成形することを特徴とする。
【選択図】なし

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【特許請求の範囲】
【請求項１】
植物から得られるリグノセルロース繊維と結晶性の樹脂組成物とを含む植物繊維樹脂複合組成物を、前記結晶性の樹脂組成物の結晶化温度を基準とした上下３０℃の範囲の温度の金型で成形することを特徴とする植物繊維樹脂複合成形品の製造方法。
【請求項２】
前記結晶性の樹脂組成物としてポリ乳酸を用い、前記金型温度を７０℃以上１３０℃以下として成形することを特徴とする請求項１記載の植物繊維樹脂複合成形品の製造方法。
【請求項３】
前記ポリ乳酸として、融解熱が１０Ｊ／ｇ以上のポリ乳酸を用いることを特徴とする請求項２記載の植物繊維樹脂複合成形品の製造方法。
【請求項４】
前記植物繊維樹脂複合組成物中に、前記リグノセルロース繊維を重量比率で２wt％以上８０wt％以下含むことを特徴とする請求項１乃至３のいずれか１項に記載の植物繊維樹脂複合成形品の製造方法。
【請求項５】
請求項１乃至４のいずれか１項に記載の植物繊維樹脂複合成形品の製造方法を用いて製造された植物繊維樹脂複合成形品。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、工業製品などの部材として適用される植物繊維樹脂複合成形品の製造方法及び植物繊維樹脂複合成形品に関する。
【背景技術】
【０００２】
プラスチックは、軽量、高強度であり、錆や腐食に強く、着色が自由、電気絶縁性に優れ、成形が容易であり、さらに大量生産が可能であるという利点を有することから、自動車、航空機、家庭用品の材料として多用されている。プラスチックの使用量が増加するに伴い廃プラスチック量も急増しており、廃プラスチックを地中に埋め、又は焼却する等して処分をしていた。しかし、埋め立て用地の確保が必要となるだけではなく、廃プラスチックの焼却により有害ガス（例えば、$CO_2$）や悪臭等が発生し、環境を汚染してしまうという問題を有していた。
【０００３】
そこで、近年、環境負荷の軽減を図るために、従来の石油を原料としたプラスチックに替えて、使用後に自然界の微生物によって分解される生分解性プラスチックの開発が急速に進められている。植物を原料とした生分解性プラスチックの代表例としてポリ乳酸が挙げられる。ポリ乳酸は、植物由来成分の分解物の一種である乳酸を重合して得られ、大量生産、低コスト化が可能であり、さらに、結晶性を有し、他の植物由来の樹脂と比較して物性が優れていること等から、有用性が高いとされている。
【０００４】
しかし、ポリ乳酸の結晶化する速度は遅く、一般的な射出成形、押出成形を用いて成形すると、結晶化が徐々にしか進まず、また、熱処理（アニール処理）などの後処理を行って結晶化する速度を速めたとしても、得られるポリ乳酸の耐熱性及び機械的特性は、既存の熱可塑性樹脂に比べて低くなっていた。
【０００５】
そこで、原材料中に無機繊維（例えば、ガラス繊維）を複合化させて、耐熱性や機械的特性を向上させた樹脂も開発されている。しかし、無機繊維は不燃物であるため、樹脂の廃棄時に焼却処理すると燃焼効率が低下し、燃焼炉の損傷、さらには焼却後の残さが増加するなどの新たな問題も生じていた。
【０００６】

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そこで、ガラス繊維などの無機繊維に替えて植物繊維を強化材とした複合材料が開発されている（特許文献１及び特許文献２参照）。

【特許文献１】特開平５－９２５２７号公報

【特許文献２】特開２００２－６９２０８号公報

【発明の開示】

【発明が解決しようとする課題】

【０００７】

しかしながら、前述した植物繊維を強化材として用いた複合材料は、廃棄時に容易に焼却でき、環境負荷を軽減できるという利点を有するが、従来の熱硬化性樹脂や熱可塑性樹脂に比べると、耐熱性、機械的強度に劣り、使用時の特性が低下するという恐れを有していた。

【課題を解決するための手段】

【０００８】

本発明は、上記課題を解決するためになされたものであり、すなわち、本発明の植物繊維樹脂複合成形品の製造方法は、植物から得られるリグノセルロース繊維と結晶性の樹脂組成物とを含む植物繊維樹脂複合組成物を、結晶性の樹脂組成物の結晶化温度を基準とした上下３０℃の範囲の温度の金型で成形することを特徴とする。

【０００９】

また、本発明の植物繊維樹脂複合成形品は、上記植物繊維樹脂複合成形品の製造方法を用いて製造されたことを要旨とする。

【発明の効果】

【００１０】

本発明の植物繊維樹脂複合成形品の製造方法によれば、使用時の耐熱性及び機械的特性に優れ、環境負荷を軽減した植物繊維樹脂複合成形品を得ることができる。

【００１１】

本発明の植物繊維樹脂複合成形品によれば、使用時の耐熱性及び機械的特性を損なうことなく、環境負荷を軽減することができる。

【発明を実施するための最良の形態】

【００１２】

以下、本発明の実施の形態に係る植物繊維樹脂複合成形品の製造方法及び植物繊維樹脂複合成形品を説明する。

【００１３】

本発明の実施の形態に係る植物繊維樹脂複合成形品の製造方法は、植物から得られるリグノセルロース繊維と、結晶性の樹脂組成物とを含む植物繊維樹脂複合組成物を、結晶性の樹脂組成物の結晶化温度を基準とした上下３０℃の範囲の金型温度として成形するものである。

【００１４】

ここで、結晶性の樹脂組成物中にリグノセルロース繊維を含めて成形している。この理由として、リグノセルロース繊維が、強化材として機能して成形品の耐熱性、機械的特性を高めることができるからである。また、リグノセルロース繊維は、その表面に存在する微細構造により、樹脂組成物の結晶核剤として作用し、樹脂組成物の結晶化を促進するからである。逆に、リグノセルロース繊維を含めずに結晶性の樹脂組成物を単独で成形した場合には、成形品の耐熱性、機械的特性が劣るだけではなく、樹脂組成物の結晶化速度が遅いため、結晶性の低い成形品しか得ることができない。実際、結晶性の樹脂組成物として、ポリエチレン、ポリエチレンテレフタレート、シンジオタクチックポリプロポレンなどを用いることができるが、ポリエチレンは結晶化温度が高く、溶融した樹脂組成物を冷却すると、融点付近で凝固しさらに結晶化する。また、ポリエチレンテレフタレート、シンジオタクチックポリプロポレンなどは、結晶化速度が遅いため、冷却速度を遅くすると融点以下の結晶化温度で結晶化するが、樹脂を急速に冷却した場合には、結晶化せず、ガラス転移温度以下で凝固して非晶（ガラス）状態となるため、成形加工が難しくなる。

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【００１５】
また、上記製造方法では、金型温度を結晶性の樹脂組成物の結晶化温度を基準とした上下３０℃の範囲内としている。この理由は、結晶性の樹脂組成物の結晶化温度を基準として下に３０℃を超えると、樹脂が急速に冷却されてしまい、樹脂を結晶化できないからであり、逆に、上に３０℃を超えると金型内で樹脂組成物が十分に凝固し難くなり、金型から取り出し難くなるからである。このため、上記範囲の温度で成形し、除々に冷却することにより、樹脂の結晶化を促進することができる。なお、結晶性の樹脂組成物を単独で用いた場合、本範囲の温度で成形すると、凝固した樹脂組成物は、柔らかく、金型から取り出すことが難しく、さらに取り出し時に変形が生じる恐れもある。これに対して、上記製造方法では、樹脂組成物中に植物から得られるリグノセルロースを含有させたため、樹脂の強度が向上し、金型から容易に取り出すことができ、さらに取り出し時の変形をも防ぐことができる。

【００１６】
従って、上記製造方法により成形された植物繊維樹脂複合成形品は、その耐熱性が高く、高温時の機械的特性が向上する。

【００１７】
ここで、リグノセルロース繊維としては、セルロースとリグニンを主成分とした材料が使用可能であり、例えば、麻類植物（例えば、ケナフ、亜麻、ラミー、大麻、ジュートなど）の靭皮から採取される繊維、麻類植物（例えば、マニラ麻、サイザル麻など）の茎又は葉の筋から採取される繊維、あるいは木材繊維を挙げることができる。これらの繊維は、セルロースとリグニンとを主成分として、その他にヘミセルロースやペクチン等の成分が含まれる。例示した繊維の中でも麻類植物の繊維を用いることが好ましい。麻類植物の繊維は、結晶性が高く、強度の高いセルロースに含有される比率が６０％以上であり、木材繊維中に含有されるセルロースの比率（３０％～５０％）に比べて高いからである。

【００１８】
また、前述した植物は、レッティングと呼ばれる浸水処理又は物理的な解繊処理によって、長さ２０㎜以上、直径３０～２００μmの繊維を容易に得ることができる。そして、これらの繊維は、長さ１～２０㎜以上、直径１０～３０μmの単繊維細胞から構成されて、パルプ化等の化学処理によって単繊維化することができる。また、前述した処理から得られる繊維以外にも、繊維状、紡糸処理によって糸状とし、さらにリグノセルロース繊維を加工処理して、シート状、不織布、織布として用いることもできる。

【００１９】
また、リグノセルロース繊維は可燃性であることから、廃棄する際の焼却時に発生する残さ量が減少し、廃棄処理が容易となる。また、廃棄後のリサイクルを考慮すると、リグノセルロース繊維は、燃焼により熱量を発生し、高効率で熱回収できるため、サーマルリサイクルが容易となる。さらに、リグノセルロース繊維は、無機繊維（ガラス繊維など）と異なり有機物であるため、加水分解処理、微生物処理、発酵処理などの処理により、エタノール、水素にまで分解されるため、ケミカルリサイクルをすることもできる。

【００２０】
樹脂組成物としては、結晶性を有するものであれば良く、特に限定されないが、結晶化する速度が遅い樹脂組成物を用いることが好ましい。このような樹脂組成物としては、例えば、ポリエチレンテレフタレート、シンジオタクチックポリプロピレン、ポリ乳酸を挙げることができ、特に、ポリ乳酸を用いることが好ましい。

【００２１】
ポリ乳酸は、トウモロコシやサツマイモなどから得られるデンプン、あるいは木本植物などから得られるセルロースを原料として、乳酸発酵して得られる乳酸を脱水縮合して得ることができる。ポリ乳酸にリグノセルロース繊維を含有して植物繊維樹脂複組成物成形品とする場合には、ポリ乳酸の結晶化温度が約１００℃であるため、金型温度を７０℃～１３０℃の範囲として成形することが好ましい。さらに結晶化速度を速くするために、金型温度を８５℃～１１５℃の範囲とすることが好ましい。

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【００２２】
また、ポリ乳酸は、L-体、D-体の光学異性体を有しており、L-体とD-体の混合比率に応じてポリ乳酸の結晶性は変化する。樹脂組成物としては、結晶性が高い樹脂組成物を用いることが好ましい。樹脂の結晶性の指標として、樹脂の融解熱を挙げることができるが、樹脂組成物としてポリ乳酸を用いた場合、リグノセルロース繊維を含有させる前の段階で、融解熱が１０Ｊ／ｇ以上のポリ乳酸を用いることが好ましい。ポリ乳酸の融解熱が１０Ｊ／ｇ未満になると、リグノセルロース繊維が結晶化剤として作用するものの、その後に結晶化が促進されず、得られる植物繊維樹脂複合成形品の結晶性が低下し、本発明の効果が相対的に低くなるからである。なお、融解熱は、結晶化した樹脂組成物を加熱しながら、熱分析（DSC）して測定することができる。また、結晶化温度は、溶融した樹脂組成物を冷却しながら、熱分析（DSC）して測定することができる。

【００２３】
また、上記植物繊維樹脂複合組成物中のリグノセルロース繊維の重量比率は、特に限定されるものではないが、２wt％～８０wt％とすることが好ましい。リグノセルロース繊維の重量比率が２wt％未満になると、強化繊維としての効果が低下し、成形金型からの取り出し時に変形し易くなるからであり、逆に、８０wt％を超えると、リグノセルロース繊維と樹脂組成物との結合力が弱まり、得られる成形品の耐熱性、機械的特性が低下するからである。なお、リグノセルロース繊維は、ポリ乳酸の融点以下の温度で軟化することが無いため、得られる植物繊維樹脂複合成形品の耐熱性、機械的特性は向上する。

【００２４】
次に、結晶性の樹脂組成物中にリグノセルロース繊維を含める方法としては、リグノセルロース繊維を溶融、あるいはエマルジョン化等により液状とした樹脂組成物に、リグノセルロース繊維を分散又は含浸する方法を用いることができる。また、リグノセルロース繊維と共に、繊維状あるいはペレット状とした樹脂組成物を混抄する方法を用いることができる。

【００２５】
例えば、樹脂組成物を溶融した後、リグノセルロース繊維と混練する方法を用いると、樹脂組成物とリグノセルロース繊維とが均一に分散されて、均一な成形体とすることができる。この場合には、一般的な混練機、押出機（例えば、一軸押出機、二軸押出機、ロール混練機など）を用いることができる。

【００２６】
成形方法としては、金型を用いて、溶融した樹脂組成物中にリグノセルロース繊維を含めた植物繊維樹脂複合組成物を成形する方法であれば、特に限定されず、上述した押出成形、射出成形、プレス成形、真空成形、圧空成形、ブロー成形、発砲成形などの方法を用いることができる。

【００２７】
成形条件は、射出成形を用いた場合、スクリュー部温度が樹脂の融点から±２０℃以内とすることが好ましい。スクリュー部温度が低くなりすぎると、ショートが発生する等して成形が不安定となり過負荷に陥りやすく、また、成形温度が高くなりすぎると熱分解が起こり、得られる成形体の強度が低下し、着色等の問題が生じるからである。

【００２８】
さらに、植物繊維樹脂複合組成物には、リグノセルロース繊維及び結晶性の樹脂組成物の他にも、他の種類の樹脂組成物、あるいは結晶化を促進する結晶核剤などの添加剤、充填剤を含めることもできる。

【００２９】
以下、さらに具体的に実施例により説明する。

【００３０】
実施例１
ケナフ茎部の外皮部分となる靭皮から得られたケナフ繊維束（平均径82μm）を用いて作成した繊維マットに、ポリ乳酸（融解熱6J/g、融点170℃、結晶化温度105℃（PL-1000,

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ミヨシ油脂（株）社製））のエマルジョンを含浸した。このとき、乾燥した時の重量比率が、ケナフ繊維束マット60wt%、ポリ乳酸40wt%となるように絞りによって調整した。ポリ乳酸を含浸した繊維マットを乾燥器により180℃で5分間加熱して、その後、すぐに金型温度90℃、圧力3.5MPaとして120秒間プレス成形した。得られた成形体を切削してASTM規格測定用サンプルを作製した。

【００３１】

実施例２

ケナフ茎部の外皮部分となる靭皮から得られたケナフ繊維束（平均径82μｍ）1wt%と、ポリ乳酸のペレット（融解熱42J/g、融点170℃、結晶化温度105℃（レイシアH-100J,三井化学工業（株）社製））98wt%と、添加剤としてタルク（竹原化学（株）社製）1wt%とを、一軸混練押出機により180℃、5分間混練して、押出しにより樹脂ペレットを作製した。得られた樹脂ペレットをシリンダ温度190℃、金型温度90、金型で120秒間保持して、射出成形した。その後、得られた成形体からASTM規格測定用サンプルを作製した。

【００３２】

実施例３

ケナフ茎部の外皮部分となる靭皮から得られたケナフ繊維束（平均径82μｍ）30wt%と、ポリ乳酸のペレット（融解熱42J/g、融点170℃、結晶化温度105℃（レイシアH-100J,三井化学工業（株）社製））70wt%とを、一軸混練押出機により180℃、5分間混練して、押出しにより樹脂ペレットを作製した。得られた樹脂ペレットをシリンダ温度190℃、金型温度90℃、金型での保持時間を120秒間として射出成形した。その後、得られた成形体からASTM規格測定用サンプルを作製した。

【００３３】

比較例１

比較例１では、実施例１と同様の方法を用いて調整したポリ乳酸を含浸した繊維マット（ケナフ繊維束マット60wt%、ポリ乳酸40wt%）を乾燥器により180℃で5分間加熱して、その後、すぐに金型温度30℃、圧力3.5MPaとして120秒間プレス成形した。得られた成形体を切削してASTM規格測定用サンプルを作製した。

【００３４】

比較例２

比較例２では、ケナフ繊維を加えずに、ポリ乳酸のペレット（融解熱42J/g、融点170℃、結晶化温度105℃（レイシアH-100J,三井化学工業（株）社製））を用いて、シリンダ温度190℃、金型温度90℃、金型での保持時間を120秒として射出成形をした。しかし、材料が柔らかすぎるため、金型から材料を取り出すことができなかった。その後、金型での保持時間を240秒として再び射出成形をしたが、依然として材料が柔らかく、金型から材料を取り出すことができなかった。

【００３５】

比較例３

比較例３では、実施例２と同様の方法を用いて調整した樹脂ペレット（ケナフ繊維束1wt%、ポリ乳酸のペレット98wt%、タルク1wt%）を用いて、シリンダ温度190℃、金型温度30℃、金型での保持時間を120秒として射出成形をした。得られた成形体を切削してASTM規格測定用サンプルを作製した。

【００３６】

比較例４

比較例４では、実施例３と同様の方法を用いて調整した樹脂ペレット（ケナフ繊維束30wt%、ポリ乳酸のペレット70wt%）を用いて、シリンダ温度190℃、金型温度30℃、金型での保持時間を120秒として射出成形をした。得られた成形体を切削してASTM規格測定用サンプルを作製した。

【００３７】

上述した実施例１～実施例３、比較例１～比較例４の各サンプルをそのままの状態として、ロックウェル硬さ(ASTM D685)及び熱変形温度(ASTM D648,荷重0.45MPa)を測定した。

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表１に、その結果を示す。

【表１】

| | 原材料 | | | | 成形条件 | | 成型品の物性 | |
|---|---|---|---|---|---|---|---|---|
| | 含有比率[wt%] | | ポリ乳酸 | | 方法 | 金型温度[℃] | ロックウェル硬さ（Mスケール） | 熱変形温度[℃] |
| | ポリ乳酸 | ケナフ繊維 | 融解熱[J/g] | 結晶化温度[℃] | | | | |
| 実施例1 | 40 | 60 | 6 | 105 | プレス成形 | 90 | 測定せず | 60 |
| 実施例2 | 98 | 1 | 42 | 105 | 射出成形 | 90 | 81 | 80 |
| 実施例3 | 70 | 30 | 42 | 105 | 射出成形 | 90 | 92 | 152 |
| 比較例1 | 40 | 60 | 6 | 105 | プレス成形 | 30 | 測定せず | 51 |
| 比較例2 | 100 | - | 42 | 105 | 射出成形 | 90 | 成形不能 | |
| 比較例3 | 98 | 1 | 42 | 105 | 射出成形 | 30 | 59 | 54 |
| 比較例4 | 70 | 30 | 42 | 105 | 射出成形 | 30 | 78 | 57 |

【００３８】

表１に示すように、実施例１と比較例１は、金型温度以外は同じ条件とし、実施例１では金型温度をポリ乳酸の結晶化温度（１０５℃）の上下３０℃の範囲内としたため、範囲外とした比較例１に比べて、熱変形温度が高くなっていることが判明した。また、実施例２と比較例３は、金型温度以外は同じ条件として、実施例２の金型温度は９０℃、比較例３の金型温度は３０℃としたため、比較例３に比べて実施例３の熱変形温度が若干高くなっていることが判明した。さらに、実施例３と比較例４は、金型温度以外は同じ条件とし、実施例３ではポリ乳酸の結晶化温度（１０５℃）の上下３０℃の範囲内とし、さらにケナフ繊維の割合を３０wt％以上としたため、金型温度を本発明の範囲外とした比較例３に

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比べて、熱変形温度が大幅に向上し、さらにロックウェル硬度も高く、耐熱性及び高温時の機械強度が向上したことが判明した。逆に、ケナフ繊維を含有しない比較例２では、材料が柔らかすぎて、金型から材料を取り出すことができなかった。この事実から、ケナフ繊維が、強化材と結晶化剤としての両機能を果たしていることが実証された。

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(72)Inventor : SUGAWARA AKIRA

## (54) METHOD FOR PRODUCING MOLDED PRODUCT OF PLANT FIBER-RESIN COMPOSITE AND THE MOLDED PRODUCT OF THE PLANT FIBER-RESIN COMPOSITE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide the molded product of a plant fiber-resin composite excellent in heat resistance and mechanical characteristics in use and reduced in environmental load and a method for producing the molded product of the plant fiber-resin composite.
SOLUTION: The plant fiber-resin composite composition containing lignocellulose fiber obtained from plants and a crystalline resin composition is molded using a mold having temperature in the range of above and below 30° C based on the crystallization temperature of the crystalline resin composition.



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最終頁に続く

(54)【発明の名称】成形体

(57)【要約】
【課題】従来のポリ乳酸組成物の成形体よりも、耐熱性に優れた成形体を提供すること。
【解決手段】少なくとも一層の乳酸系ポリマーを含む乳酸系樹脂組成物からなる層と、少なくとも一層の乳酸系ポリマー以外の耐熱温度（ＨＤＴ）（ＩＳＯ７５に準拠：荷重０．４５ＭＰａ）が７０℃以上である耐熱性熱可塑性樹脂を含む耐熱性熱可塑性樹脂組成物からなる層とを有する多層シートを二次成形することにより得られる成形体。
【選択図】なし

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【特許請求の範囲】
【請求項１】
少なくとも一層の乳酸系ポリマーを含む乳酸系樹脂組成物からなる層と、
少なくとも一層の乳酸系ポリマー以外の耐熱温度（ＨＤＴ）（ＩＳＯ７５に準拠：荷重０．４５ＭＰａ）が７０℃以上である耐熱性熱可塑性樹脂を含む耐熱性熱可塑性樹脂組成物からなる層とを有する多層シートを二次成形することにより得られる成形体。
【請求項２】
前記多層シートが三層以上の層構造を有し、かつ少なくとも一方の最外層が耐熱性熱可塑性樹脂組成物からなる層であることを特徴とする請求項１に記載の成形体。
【請求項３】
前記乳酸系樹脂組成物がさらに透明核剤を含むことを特徴とする請求項１または２に記載の成形体。
【請求項４】
厚みが１５０～４００μｍの部分のヘイズ（ＪＩＳ　Ｋ６７１４に準拠）が０．１～１０％の請求項１～３のいずれかに記載の成形体。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は多層シートを二次成形することにより得られる成形体に関する。
【背景技術】
【０００２】
従来、プラスチックから作られる成形体の材料としては、ポリスチレン、ポリ塩化ビニル、ポリプロピレン、ポリエチレンテレフタレート樹脂が使用されている。かかる樹脂から製造された成形体は透明性に優れているものもあるが、廃棄する際その処理方法を誤るとゴミの量を増加させる。さらに、自然環境下では殆ど分解しないため、埋設処理すると半永久的に地中に残留する。
【０００３】
近年、熱可塑性樹脂で生分解性を有するポリマーとして、乳酸系ポリマー、例えば、ポリ乳酸や、乳酸とその他のヒドロキシカルボン酸とのコポリマーなどが開発されている。乳酸系ポリマーは、動物の体内で数カ月から１年以内に１００％生分解し、また、土壌や海水中に置かれた場合、湿った環境下では数週間で分解を始め、約１年から数年で消滅し、さらに、その分解生成物は、人体に無害な乳酸と二酸化炭素と水になるという特性を有している。
【０００４】
しかしながら、ポリ乳酸の透明な成形体は、通常、ガラス転移温度（Ｔｇ）が低く非晶性であるがゆえに耐熱性に劣る。例えば、非晶性ポリ乳酸容器は透明性に優れているが耐熱性が低く、熱湯や電子レンジを使用することができず、用途が限定されていた。また、耐熱性を向上させるために、成形加工時に結晶化温度付近に保持した金型内に充填することにより、あるいは、成形後に非晶性の成形体を熱処理（アニール）等することにより、結晶化度をあげると、通常、光を散乱する原因となる光の波長と同程度以上の大きさの結晶（例えば、球晶）が急速に成長して、成形体は不透明となってしまう。
【０００５】
そこで、上記乳酸系ポリマーに結晶核剤を添加して結晶化を促進することにより、シートや成形体の耐熱性を向上することが検討されてきたが、樹脂そのものの透明性を阻害することなく耐熱性を付与することは困難であった。
【０００６】
例えば、特開２００２－１４６１７０号公報（特許文献１）には、可塑剤と結晶核剤とを必須成分とし、可塑化されたポリ乳酸樹脂に特定の結晶性を付与することにより、実用性の高いフィルムが得られることが記載されている。しかしながら、この方法によると、添加した結晶核剤の粒子径が大きいこと、あるいはその添加量が多いことから、透明性が

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著しく低下し、良好な透明性を有するシートや成形体を得ることは困難である。

【０００７】

また、特開平９－２７８９９１号公報（特許文献２）には、脂肪族カルボン酸アミド、脂肪族カルボン酸塩、脂肪族アルコールおよび脂肪族カルボン酸エステルからなる群より選択された少なくとも１種の透明核剤と乳酸系ポリマーとからなる組成物を成形し、成形時または成形後に熱処理することにより、透明性および結晶性が付与された成形体およびその製造方法が記載されている。しかしながら、この方法は、例えば、熱成形の場合は成形時に該樹脂組成物が結晶化する温度に保持された金型に接触させる必要があり、設備面や経済性の点で工業的且つ汎用的に容易に実施できる技術とは言い難い。

【０００８】

更に、核剤無添加の場合はあまり進行せず結晶化度５％以下を示すが、該樹脂組成物からなるシートを室温の金型を用いて熱成形すると、予熱時に結晶化が進行し得られた成形体は結晶化度２０～３０％を示す。しかしながら、熱成形体の耐熱性は、結晶化度の大きい成形体よりも寧ろ結晶化度の小さい成形体が高い値を示す事が判り、必ずしも結晶化度の高い成形体が耐熱性が良いとは限らない。

【特許文献１】特開２００２－１４６１７０号公報

【特許文献２】特開平９－２７８９９１号公報

【発明の開示】

【発明が解決しようとする課題】

【０００９】

乳酸系樹脂組成物からなる層を有する多層シートを二次成形することにより得られる、耐熱性に優れた成形体を提供することを目的とする。

【課題を解決するための手段】

【００１０】

本発明者らは、上記課題を達成するために鋭意検討した結果、乳酸系樹脂組成物からなる層と、熱可塑性樹脂組成物からなる層とを有する積層体を二次成形することにより得られる成形体は、耐熱性に優れることを見いだし本発明を完成するに至った。

【００１１】

すなわち本発明の成形体は、

少なくとも一層の乳酸系ポリマーを含む乳酸系樹脂組成物からなる層と、

少なくとも一層の乳酸系ポリマー以外の耐熱温度（ＨＤＴ）（ＩＳＯ７５に準拠：荷重０．４５ＭＰａ）が７０℃以上である耐熱性熱可塑性樹脂を含む耐熱性熱可塑性樹脂組成物からなる層とを有する多層シートを二次成形することにより得られる。

【００１２】

前記多層シートが三層以上の層構造を有し、かつ少なくとも一方の最外層が耐熱性熱可塑性樹脂組成物からなる層であってもよい。

前記乳酸系樹脂組成物がさらに透明核剤を含んでいることが好ましい。

【００１３】

前記成形体は厚みが１５０～４００μｍの部分のヘイズ（ＪＩＳ　Ｋ６７１４に準拠）が０．１～１０％であることが好ましい。

【発明の効果】

【００１４】

本発明によれば、少なくとも一層の乳酸系樹脂組成物からなる層と、少なくとも一層の耐熱性熱可塑性樹脂組成物からなる層とを有する多層シートを二次成形することにより得られる、耐熱性に優れた成形体を提供することができる。

【発明を実施するための最良の形態】

【００１５】

以下、本発明に係る成形体について詳細に説明する。

本発明の成形体は、少なくとも一層の乳酸系ポリマーを含む乳酸系樹脂組成物からなる層と、少なくとも一層の乳酸系ポリマー以外の耐熱温度（ＨＤＴ）（ＩＳＯ７５に準拠：

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荷重０．４５ＭＰａ）が７０℃以上である耐熱性熱可塑性樹脂を含む耐熱性熱可塑性樹脂組成物からなる層とを有する多層シートを二次成形することにより得られる。

【００１６】

＜乳酸系ポリマー＞

本発明に用いる乳酸系樹脂組成物に含まれる乳酸系ポリマーは、乳酸単位を５０モル％以上、好ましくは７５モル％以上含むポリマーであり、具体的には、（１）ポリ乳酸、または乳酸－他の脂肪族ヒドロキシカルボン酸コポリマー、（２）多官能多糖類および乳酸単位を含む乳酸系ポリマー、（３）脂肪族多価カルボン酸単位、脂肪族多価アルコール単位および乳酸単位を含む乳酸系ポリマー、ならびに（４）これらの混合物である。これらの中では、使用時の透明性および耐熱性等を考慮すると、好ましくはポリ乳酸および乳酸－他の脂肪族ヒドロキシカルボン酸コポリマーであり、さらに好ましくはポリ乳酸である。なお、乳酸にはＬ－乳酸とＤ－乳酸とが存在するが、本発明において、単に乳酸という場合は、特にことわりがない限り、Ｌ－乳酸およびＤ－乳酸の両方を意味する。

【００１７】

上記乳酸系ポリマーの原料としては、乳酸類およびヒドロキシカルボン酸類が用いられる。乳酸類としては、Ｌ－乳酸、Ｄ－乳酸、これらの混合物または乳酸の環状２量体であるラクタイドを使用することができる。なお、高い結晶性を発現するためには、このような乳酸類を原料とする乳酸系ポリマーにおいて、Ｌ－乳酸含有率またはＤ－乳酸含有率が大きい方が好ましい。具体的には、乳酸単位中におけるＬ－乳酸またはＤ－乳酸の含有率が、好ましくは９０％以上、より好ましくは９５％以上、特に好ましくは９８％以上である。

【００１８】

また、上記乳酸類と併用できるヒドロキシカルボン酸類としては、炭素数２～１０のヒドロキシカルボン酸類が好ましい。具体的には、グリコール酸、３－ヒドロキシ酪酸、４－ヒドロキシ酪酸、４－ヒドロキシ吉草酸、５－ヒドロキシ吉草酸、６－ヒドロキシカプロン酸などを好適に使用することができる。また、ヒドロキシカルボン酸の環状エステル中間体、例えば、グリコール酸の２量体であるグリコライドや、６－ヒドロキシカプロン酸の環状エステルであるε－カプロラクトンも使用できる。原料としての乳酸類とヒドロキシカルボン酸類との混合物は、得られるコポリマー中の乳酸含有率が５０％以上、好ましくは７５％以上になるように、種々の組み合わせで使用することができる。

【００１９】

上記乳酸系ポリマーを得るためには、公知公用の方法を用いることができる。例えば、上記原料を直接脱水重縮合する方法や、上記乳酸類やヒドロキシカルボン酸類の環状２量体、例えばラクタイドやグリコライド、あるいはε－カプロラクトンのような環状エステル中間体を開環重合させる方法などが挙げられる。

【００２０】

直接脱水重縮合して製造する場合、原料である乳酸類または乳酸類とヒドロキシカルボン酸類との混合物を、好ましくは有機溶媒の存在下で共沸脱水縮合して重合することにより、本発明に適した強度を持つ高分子量の乳酸系ポリマーが得られる。特に、有機溶媒としてフェニルエーテル系溶媒を用い、共沸により留出した溶媒から水を除去し、実質的に無水の状態にした溶媒を反応系に戻すことが好ましい。

【００２１】

乳酸系ポリマーの重量平均分子量（Ｍｗ）は、好ましくは３万～５００万、より好ましくは５万～１００万、さらに好ましくは１０万～３０万、特に好ましくは１０万～２０万である。また、その分散度（Ｍｗ／Ｍｎ）は、２～１０、好ましくは２～８、より好ましくは２～６、さらに好ましくは２～４、特に好ましくは２～３である。乳酸系ポリマーの重量平均分子量（Ｍｗ）や分散度（Ｍｗ／Ｍｎ）が前記範囲にあることにより、結晶化の速度が早く、成形可能な乳酸系樹脂組成物が得られる。

【００２２】

＜乳酸系樹脂組成物＞

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本発明で用いる乳酸系樹脂組成物とは、上述した乳酸系ポリマーを含む組成物である。乳酸系樹脂組成物は必要に応じてさらに各種改質剤を含んでいても良い。改質剤としては例えば、透明核剤、滑剤、アンチブロッキング剤、離型剤、結晶核剤、結晶化促進剤、可塑剤、静電防止剤、防曇剤、紫外線吸収剤、酸化防止剤、耐衝撃性改良剤などが挙げられる。これらは１種単独でも、２種以上が含まれていてもよい。また乳酸系樹脂組成物が改質剤を含む場合には乳酸系ポリマー１００重量部に対して通常は２０重量部以下の範囲で含まれていることが好ましい。

【００２３】

（透明核剤）

本発明における透明核剤とは、結晶化の際に核剤となるものでかつ透明性を付与するものである。具体的には、エチレンビスステアリン酸アミド、エチレンビスラウリン酸アミド、エチレンビスオレイン酸アミドが挙げられる。これらは一種類で用いても良く、また二種類以上の混合物として用いても良い。

【００２４】

（滑剤）

本発明における滑剤とは、流動性や成形時（シート温度１００℃前後）の伸び率を向上させ得るものをいう。滑剤としては有機系滑剤であっても無機系滑剤であってもよい。

【００２５】

有機系滑剤の例としては、流動パラフィン、マイクロクリスタリンワックス、天然パラフィン、合成パラフィン、ポリエチレン等の脂肪族炭化水素系滑剤；ステアリン酸、ラウリン酸、ヒドロキシステアリン酸、硬化ひまし油等の脂肪酸系滑剤；ステアリン酸鉛、ステアリン酸カルシウム、ヒドロキシステアリン酸カルシウム等の炭素数１２～３０の脂肪酸金属塩である金属石鹸系滑剤；モンタンワックス等の長鎖エステルワックス類；炭素数１２～３０の高級脂肪族アルコール化合物；炭素数１２～３０の高級脂肪族アミド化合物、およびこれらを複合した複合滑剤などが挙げられる。中でも、炭素数１２～３０の高級脂肪族アルコール化合物が好ましく、ステアリルアルコールが特に好ましい。

【００２６】

無機系滑剤の例としては、シリカ、タルク、炭酸カルシウム、クレー等のフィラーおよびシリコーンオイルが挙げられる。

無機系滑剤としてフィラーを用いる場合にはその平均粒径は通常は５μｍ以下、好ましくは４μｍ以下、より好ましくは３μｍ以下、さらに好ましくは２μｍ以下である。平均粒径が５μｍを超える粒径になると多層シートの表面に微細な凹凸が生じ外観が不透明になる場合がある。

【００２７】

得られる成形体に高度に透明性が必要な場合には、好ましくは平均粒径７ｎｍ～２００ｎｍ、より好ましくは７ｎｍ～２００ｎｍ、さらに好ましくは７ｎｍ～５０ｎｍのシリカを用いることが望ましい。また、そのシリカは$SiO_2$を９５％以上含むことが好ましく、さらに、該$SiO_2$が無水シリカであることがより好ましい。

【００２８】

シリコーンオイルは成形体の金型からの離形成を同時に付与することができるため好ましい。シリコーンオイルとしては特に限定は無く例えば、アルキル変性シリコーンオイル、メチルスチリル変性シリコーンオイル、ポリエーテル変性シリコーンオイル、高級脂肪酸エステル変性シリコーンオイル、高級脂肪酸アルコキシ変性シリコーンオイル、高級脂肪酸含有シリコーンオイル、メタクリル変性シリコーンオイル、フッ素変性シリコーンオイルなどを用いることができる。

【００２９】

またシリコーンオイルを用いる場合には通常、オストワルト法を用いて測定した際の２５℃における粘度が、１０～１０，０００ｃｓの範囲、好ましくは、１００～１，０００ｃｓの範囲にあるものを用いる。

【００３０】

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なお、滑剤として有機系滑剤を用いる場合には１種単独で用いても２種以上を用いても良く、滑剤として無機系滑剤を用いる場合にはそれぞれ１種単独で用いても２種以上を用いても良い。また有機滑剤と無機系滑剤とを用いてもよい。

【００３１】

上記滑剤を用いる場合の使用量は乳酸系ポリマー１００重量部に対して通常は０．０１～５重量部、好ましくは０．１～３重量部、より好ましくは０．３～１重量部である。添加量が上記範囲内にあると流動性や成形時（シート温度１００℃前後）の伸び率を向上させることができる。

【００３２】

（アンチブロッキング剤）

本発明におけるアンチブロッキング剤としては、公知公用のものを用いることができ、無機フィラーなどが好適に用いられる。このような無機フィラーとしては、例えば、シリカ、炭酸カルシウム、チタニア、マイカ、タルク等が挙げられ、特にシリカが好ましい。

【００３３】

また、上記アンチブロッキング剤の平均粒径は５μｍ以下、好ましくは４μｍ以下、より好ましくは３μｍ以下、さらに好ましくは２μｍ以下である。平均粒径が５μｍを超えるとフィルムの表面に微細な凹凸が生じ外観が不透明になる場合がある。

【００３４】

得られる成形体に高度に透明性が必要な場合には、好ましくは平均粒径７ｎｍ～２０００ｎｍ、より好ましくは７ｎｍ～２００ｎｍ、さらに好ましくは７ｎｍ～５０ｎｍのシリカを用いることが望ましい。また、そのシリカは$SiO_2$を９５％以上含むことが好ましく、さらに、該$SiO_2$が無水シリカであることがより好ましい。

【００３５】

上記アンチブロッキング剤の添加量は、乳酸系ポリマー１００重量部に対して０．０１～３重量部、好ましくは０．０５～２重量部、さらに好ましくは０．０５～１重量部の範囲の量で用いられる。添加量が過少であると、アンチブロッキング剤の効果が発現し難くなり、逆に添加量が過大であると、フィルムの外観、特に透明性を低下させる場合がある。

【００３６】

（離型剤）

本発明では成形加工時の成形性を向上するために、公知公用の離型剤を添加することもできる。用いられる離型剤としては、乳酸系樹脂組成物の特徴を損なわない限り何等制限はない。例えば、シリコン誘導体類、テフロン（登録商標）誘導体類、脂肪族カルボン酸類、脂肪族カルボン酸金属塩類、脂肪族アルコール類などが挙げられる。特に、離型剤効果の高いシリコン誘導体類や脂肪族カルボン酸類が好ましい。

【００３７】

上記シリコン誘導体類としては、ジメチルシリコーンオイルが特に好ましく、その溶液粘度は、０．５～５０万センチストークス、好ましくは１～１万センチストークス、より好ましくは５～５０００センチストークス、さらに好ましくは５～１０００センチストークスである。例えば、ＫＦ９６（商品名；信越化学（株）製）、ＫＦ６９（商品名；信越化学（株）製）、ＫＭＰ１１０（商品名；信越化学（株）製）が挙げられる。

【００３８】

上記脂肪族カルボン酸類は、炭素数８～３０の脂肪族カルボン酸、好ましくは炭素数１０～２６の脂肪族カルボン酸、より好ましくは炭素数１２～２２の脂肪族カルボン酸である。

【００３９】

上記離型剤は、乳酸系ポリマー１００重量部に対して、０．０１重量部～１重量部、好ましくは０．０５重量部～０．８重量部、より好ましくは０．１重量部～０．５重量部の範囲の量で用いられる。

【００４０】

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（結晶核剤）

本発明における結晶核剤とは、結晶性の熱可塑性樹脂組成物に添加し、ある条件下で加熱処理を行った際に結晶核となり、結晶核形成を速め、その結果結晶化速度が速くなる効果を有するものおよび/又は結晶サイズを小さくし透明性を維持する効果を示すものである。本発明で用いられる結晶核剤としては、無機結晶核剤と有機結晶核剤が挙げられる。

【００４１】

無機結晶核剤としては、乳酸系ポリマーの結晶化速度を上げる効果のある化合物であれば何等制限はなく用いる事ができ、例えばタルク、カオリン、クレー等の珪酸塩化合物が挙げられる。

【００４２】

無機核剤の添加量は、乳酸系ポリマー１００重量部に対して、０．０５～３重量部、好ましくは０．１～２．０重量部、より好ましくは０．１～１．０重量部である。

一方有機結晶核剤としては無機結晶核剤と同様、乳酸系ポリマーの結晶化速度を上げる効果のある化合物、更には結晶の大きさおよび数を制御して透明性を保持することのできる有機化合物、が好ましく用いる事ができ、例えばアミド結合を持つ脂肪族カルボン酸アミドを含んでなる有機化合物が挙げられる。

【００４３】

特に乳酸系ポリマーがポリ乳酸の場合、エチレンビスステアリン酸アミド、エチレンビスラウリン酸アミド、エチレンビスオレイン酸アミドおよびヘキサメチレンビスベヘニン酸アミドが好ましい。

【００４４】

また、乳酸系ポリマーが乳酸と他の脂肪族ヒドロキシカルボン酸との共重合体や、乳酸単位、他の脂肪族多価カルボン酸単位および脂肪族多価アルコール単位を含む共重合体の場合は、ステアリン酸アミド、オレイン酸アミド、エルカ酸アミドなどの脂肪族カルボン酸モノアミドが好ましい。

【００４５】

これ等の有機結晶核剤は、１種単独で用いても、２種以上を組み合わせて用いてもよい。

また有機核剤の添加量は乳酸系ポリマー１００重量部に対して、０．０５～３重量部、好ましくは０．１～２．０重量部、より好ましくは０．１～１．５重量部、更に好ましくは０．１～１．０重量部、より好ましくは０．２～０．８重量部である。

【００４６】

（結晶化促進剤）

本発明における結晶化促進剤とは、上記乳酸系樹脂組成物を何等かの方法（例えば、熱処理）により結晶化させた時に、結晶の成長速度を速め、その結果結晶化速度が速くなる作用を有するものをいう。

【００４７】

なお、結晶化促進剤は、本発明の成形体が透明性が必要な用途に用いられる場合には、乳酸系ポリマーの透明性を実質上損なわない効果を有することが好ましい。

上記結晶化促進剤としては、例えば、ジ-ｎ-オクチルフタレート、ジ-２-エチルヘキシルフタレート、ジベンジルフタレート、ジイソデシルフタレート、ジトリデシルフタレート、ジウンデシルフタレート等のフタル酸誘導体、ジオクチルイソフタレート等のイソフタル酸誘導体、ジ-ｎ-ブチルアジペート、ジオクチルアジペート等のアジピン酸誘導体、ジ-ｎ-ブチルマレエート等のマレイン酸誘導体、トリ-ｎ-ブチルシトレート等のクエン酸誘導体、モノブチルイタコネート等のイタコン酸誘導体、ブチルオレート等のオレイン酸誘導体、グリセリンモノリシノレート等のリシノール酸誘導体、トリクレジルフォスフェート、トリキシレニルフォスフェート等のリン酸エステル、ポリエチレンアジペート、ポリアクリレートアセチルクエン酸トリブチル等のヒドロキシ多価カルボン酸エステル類、グリセリントリアセテート、グリセリントリプロピオネート等の多価アルコールエステル類、ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール

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誘導体、ベンジル＝２－（２－メトキシエトキシ）エチル＝アジパートなどが挙げられる。

【００４８】

特に乳酸系ポリマーがポリ乳酸の場合は、少量で結晶化速度を促進する効果を示し、安価でかつ容易に入手できるクエン酸誘導体、ポリアルキレングリコール誘導体、ヒドロキシ多価カルボン酸エステル類および多価アルコールエステル類が好ましく用いる事ができる。

【００４９】

具体的には、ポリエチレングリコール、ＡＴＢＣ（商品名；ジェイ・プラス（株）製）、ダイファッティー１０１（商品名；大八化学（株）製）、リケマールＰＬ－７１０（商品名；理研ビタミン（株）製）およびラクトサイザーＧＰ－４００１（商品名；荒川化学（株）製）等は、安価でかつ容易に入手でき、結晶化促進効果も高いことから、好ましく用いることができる。

【００５０】

本発明の結晶化促進剤の添加量は、乳酸系ポリマー１００重量部に対して、０．１重量部～７重量部、好ましくは０．５～７重量部、より好ましくは１～５重量部、さらに好ましくは１～３重量部である。

【００５１】

（耐衝撃性改良剤）

本発明では成形体の耐衝撃性を向上するために、公知公用の耐衝撃改良剤を添加することもできる。用いられる耐衝撃改良剤としては、乳酸系樹脂組成物の特徴を損なわない限り何ら制限はない。例えば、生分解性を有する耐衝撃性改良剤や非生分解性の熱可塑性エラストマーなどが挙げられる。特に、生分解性を有する耐衝撃性改良剤が好ましい。

【００５２】

生分解性の耐衝撃性改良剤としては、たとえば、プラメートＰＤ－１５０（商品名；大日本インキ化学社製）やプラメートＰＤ－３５０（商品名；大日本インキ化学社製）などが挙げられる。非生分解性の熱可塑性エラストマーとしては、たとえば、タフマー（商品名；三井化学社製）、シンジオタクティックポリプロピレン、エチレン－プロピレン－ジエンゴム、スチレン－ブタジエン－ブチレン－スチレン系のＳＢＢＳラバー、イミノ変性したＳＢＢＳラバー、スチレン－エチレン－ブチレン－スチレン系のＳＥＢＳラバー、イミノ変性したＳＥＢＳラバー等のオレフィン系エラストマーもしくはラバーや、メタブレン（商品名：三菱レイヨン社製）等のシリコン系ラバーなどが挙げられる。

【００５３】

上記耐衝撃性改良剤は、一種単独で用いても、２種以上を組み合わせて用いてもよい。上記耐衝撃改良剤の添加量は、用途に応じて適宜選択することができるが、乳酸系ポリマー１００重量部に対して、０．１重量部～２０重量部、好ましくは１重量部～１５重量部、より好ましくは３重量部～１０重量部の範囲の量で用いられる。

【００５４】

＜乳酸系樹脂組成物の製造方法＞

本発明の乳酸系樹脂組成物は、上述の乳酸系ポリマーに、必要に応じて上述の改質剤を混合することにより得られる。各成分の混合は、公知公用の方法や混練技術を適用できる。例えば、

（１）パウダー状もしくはペレット状の乳酸系ポリマー、必要に応じて他の改質剤をリボンブレンダーなどで一括混合した後、２軸押出機で組成物を加熱溶融しながら押出しペレット化する方法；

（２）パウダー状もしくはペレット状の乳酸系ポリマーを押出ペレット化する際に、必要に応じて他の改質剤を、サイドフィードや液体注入ポンプで押出し機のシリンダー内に添加混合する方法；

（３）予め必要に応じて他の改質剤を、高濃度に押出しペレット化したペレット（マスターバッチ）を製造した後、そのマスターバッチを、パウダー状もしくはペレット状の乳酸系ポリマーでドライブレンド等により希釈して成形体を加工する方法；

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（４）上記方法を組み合わせて混合する方法
などが挙げられる。
なお、必要に応じて他の改質剤をマスターバッチとして添加する場合、各改質剤毎のマスターバッチ、あるいは２種以上の改質剤のマスターバッチとして添加してもよく、その方法に何等制限はない。また、マスターバッチとして添加する際、乳酸系ポリマーとの混合比率は、マスターバッチ／乳酸系ポリマーの重量比が１／１００～１／２、好ましくは１／５０～１／３、より好ましくは１／３０～１／５、特に好ましくは１／３０～１／１０である。

【００５５】

＜耐熱性熱可塑性樹脂＞

本発明において耐熱性熱可塑性樹脂とは前述の乳酸系ポリマー以外の熱可塑性樹脂であり、かつ耐熱温度（ＨＤＴ）（ＩＳＯ７５に準拠：荷重０．４５ＭＰａ）が７０℃以上の樹脂である。

【００５６】

本発明の成形体に透明性が必要な場合には、非晶性の樹脂が好ましく、例えばポリスチレン、ポリメチルメタクリレート（ＰＭＭＡ）、ポリカーボネート等を用いることができる。

【００５７】

中でも乳酸系樹脂組成物からなる層との接着性、成型加工温度の観点からＰＭＭＡが好ましい。

＜耐熱性熱可塑性樹脂組成物＞

本発明で用いる耐熱性熱可塑性樹脂組成物とは、上述した耐熱性熱可塑性樹脂を含む組成物である。耐熱性熱可塑性樹脂組成物は必要に応じてさらに各種改質剤を含んでいても良い。用いることが可能な改質剤としては上述の乳酸系樹脂組成物に用いられる改質剤と同様である。
また耐熱性熱可塑性樹脂組成物が改質剤を含む場合には耐熱性熱可塑性樹脂１００重量部に対して通常は２０重量部以下の範囲で含まれていることが好ましい。

【００５８】

＜耐熱性熱可塑性樹脂組成物の製造方法＞

本発明に用いる耐熱性熱可塑性樹脂組成物は、上述の耐熱性熱可塑性樹脂に必要に応じて上述の改質剤を混合することにより得られる。耐熱性熱可塑性樹脂組成物は上述の乳酸系樹脂組成物の製造方法と同様に、公知公用の方法や混練技術を適用できる。

【００５９】

＜多層シート＞

本発明に用いる多層シートは、少なくとも一層の乳酸系ポリマーを含む乳酸系樹脂組成物からなる層と、少なくとも一層の乳酸系ポリマー以外の耐熱性熱可塑性樹脂を含む耐熱性熱可塑性樹脂組成物からなる層とを有する。

【００６０】

本発明に用いる多層シートの層構造としては、少なくとも１層が乳酸系樹脂組成物からなる層（ｘ）であり、かつ少なくとも１層が耐熱性熱可塑性樹脂組成物からなる層（ｙ）であれば、特に限定されず、例えば、層（ｘ）／層（ｙ）の２層構造、層（ｙ）／層（ｘ）／層（ｙ）、層（ｘ）／層（ｙ）／層（ｘ）、の３層構造などの構造をとることができ、成形体の用途によって適宜選択すればよい。

【００６１】

また上述の乳酸系樹脂組成物や耐熱性熱可塑性樹脂以外の層を設けても良い。つまり、本発明の成形体にガスバリア性が必要な場合には、ガスバリア性を有する樹脂、例えばエチレン-ビニルアルコール共重合樹脂（ＥＶＯＨ）等を用いることができる。

【００６２】

他にも成形体が三層以上の多層構造であり、各層の接着性が不足する場合には、接着層としてマレイン酸変性ポリオレフィンを用いることができる。

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本発明の成形体に耐熱性を付与する観点から、少なくとも一方の最外層が耐熱性熱可塑性樹脂層からなる層（ｙ）であることが好ましく、両方の最外層が耐熱性熱可塑性樹脂組成物からなる層（ｙ）であることがより好ましい。

【００６３】

また、上述した改質剤を乳酸系樹脂組成物および／または耐熱性熱可塑性樹脂組成物に添加する場合、全ての層に添加しても良く、選択した任意の層に添加しても良く、その目的によって適宜選択できる。

【００６４】

例えば、シートの滑り性を付与するためには、滑剤やアンチブロッキング剤を最外層にのみ添加することが好ましく、比較的少ない量で効率的に滑り性を発現できる。

層の厚み構成としては、２層構造の場合、層（ｘ）／層（ｙ）の厚みの比ｘ／ｙは、０．０５～０．９５／０．９５～０．０５、好ましくは０．２～０．８／０．８～０．２、より好ましくは０．３～０．７／０．７～０．３である。また層（ｙ）／層（ｘ）／層（ｙ）の３層構造の場合、厚みの比ｙ／ｘ／ｙは、０．０５～０．６／０．０５～０．９／０．０５～０．６、好ましくは０．０５～０．５／０．２～０．８５／０．０５～０．５より好ましくは０．１～０．４／０．３～０．８／０．１～０．４である。

【００６５】

本発明に用いる多層シートは、公知公用の押出し機や押出し技術で製造することができる。また、本発明に用いる多層シートは必要に応じて延伸加工が施されていても良い。

本発明に用いる多層シートは、Ｔダイが装着された押出機を用いる溶融押出法によりシート状に成形することが好ましい。この際、異なる樹脂組成物を、別々にシート化した後に接着してもよいし、また、マルチマニホールドダイまたはフィードブロックを備えた押出機を用いて、共押出してもよい。また、得られた多層シートをロール延伸によって流れ方向に延伸することにより延伸加工を施しても良い。さらに、テンター延伸によって横方向に延伸してもよいし、横延伸後、緊張下で熱処理してもよい。

【００６６】

本発明に用いる多層シートは、必要に応じて多層シート表面に帯電防止性、防曇性、粘着性、ガスバリヤー性、密着性および易接着性などの機能を有する層をコーティングにより形成することができる。例えば、多層シートの片面もしくは両面に、帯電防止剤を含む水性塗工液を塗布して乾燥することによって帯電防止層を形成することができる。また、本発明の多層シートは、必要に応じて、他樹脂および他シートをラミネートすることにより、帯電防止性、防曇性、粘着性、ガスバリヤー性、密着性および易接着性などの機能を有する層を形成することができる。その際、押出ラミネーション、ドライラミネーションなどの公知の方法を用いることができる。

＜成形体＞

本発明の成形体は、上述の多層シートを熱成形することにより得られ耐熱性に優れている。

本発明において熱成形とは、上述した多層シートを加熱軟化させて後適宜外力で片面に圧着して冷却固化する成形方法のことであり、具体的には真空成形、真空圧空成形、熱板加熱圧空成形などの方法が挙げられる。場合によってプラグを用いる場合もある。

【００６７】

本発明の成形体は上述した多層シートを用いることにより耐熱性に優れる。耐熱性の評価としては、例えばカップ状の成形体を恒温器中で一定の温度で２時間保持し、その前後でカップの高さを測定し、カップの寸法変化を計算することにより、寸法変形が少ないほど耐熱性に優れると評価することができる。一般に成形体を輸送、保管する際など、夏場などは外気温の上昇にともない、コンテナ内や倉庫内は６０℃程度まで上昇する場合がある。このため温度６５℃での寸法変化が３％以下であることが好ましく、２％以下がより好ましい。上記範囲内では成形体の輸送、保管の際に耐熱性が問題になることがなく好ましい。

【００６８】

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また本発明の成形体は熱可塑性樹脂組成物として、ポリスチレン、ポリメチルメタクリレート（ＰＭＭＡ）、ポリカーボネート等を用いることにより透明性にも優れる。具体的には、厚みが１５０～４００μｍの部分の成形体のヘイズ（ＪＩＳ　Ｋ６７１４に準じて、東京電色製Ｈａｚｅ　Ｍｅｔｅｒを用いて測定）は、通常は０．１～１０％、好ましくは０．１～８％、より好ましくは０．１～７％である。

【００６９】

本発明の成形体は、乳酸系ポリマーの特徴である高い透明性と高い耐熱性を両立することができるため、例えば、プリン、ジャムおよびカレー容器等のホットフィル容器、食品トレー、ブリスター容器、ならびに、クリアケース等の一般包装用容器など、透明性と耐熱性が要求される用途にも広く用いることができる。

【００７０】

［実施例］

以下、実施例に基づいて本発明を具体的に説明するが、本発明はこれら実施例に何ら限定されるものではない。

なお、実施例における各種物性は下記の方法で測定・評価した。

【００７１】

＜耐熱性＞

成形したカップの耐熱性は６５℃の恒温器中で２時間保持し、その前後でカップの高さを測定し、カップの寸法変化を計算し、寸法変形が少ないほど耐熱性に優れると評価した。

【００７２】

寸法変化は以下の計算式により求めた。

寸法変化（％）＝（Ｈ０－Ｈ１）／Ｈ０×１００

Ｈ０：恒温器中で保持する前のカップの高さ

Ｈ１：恒温器中で２時間保持した後のカップの高さ

＜透明性（ヘイズ）＞

成形体（カップ）の側面から、縦５ｃｍ×横２ｃｍのカットサンプルを採取し、このカットサンプルについて、厚み及びヘイズを測定した。ヘイズは、ＪＩＳ　Ｋ６７１４に準じて、東京電色製Ｈａｚｅ　Ｍｅｔｅｒを用いて測定した。

【実施例１】

【００７３】

ポリ乳酸樹脂（ＬＡＣＥＡ（登録商標）：Ｈ－４００、三井化学（株）製）１００重量部とポリメチルメタクリレート樹脂（アクリペットＶ、三菱レイヨン製）（耐熱温度（ＨＤＴ）＝９７℃（ＩＳＯ７５に準拠し荷重０．４５ＭＰａで測定））とを、樹脂温度が２２０℃に設定された２層Ｔ－ダイ製膜機（スクリュー径６５ｍｍφ、ダイス幅５００ｍｍ）のそれぞれ別のホッパーへ供給し、各層の厚みを、外層１（乳酸系樹脂組成物層）／外層２（ＰＭＭＡ層）＝７０／３０となるようにして、温度を３０℃に調整したキャストロール上に溶融樹脂を押出し、厚み１１００μｍの２層シートを得た。

【００７４】

得られた２層シートを、表面温度が１００℃になるように予熱した後、金型とプラグを用いて、真空圧空熱成形を行い成形体としてカップを得た。金型は、上部口径１００ｍｍ、底部口径６０ｍｍ、高さ１２０ｍｍ、絞り比１．２のカップ状の金型を用いた。

【００７５】

成形したカップの耐熱性および透明性を評価した。その結果を表１に示す。

【実施例２】

【００７６】

ポリ乳酸樹脂（ＬＡＣＥＡ（登録商標）：Ｈ－４００、三井化学（株）製）１００重量部と、エチレンビスステアリン酸アミド（アルフロー　Ｈ－５０Ｐ、日本油脂（株）製）０．５重量部とをヘンシェルミキサーにて混合後、押出機シリンダー設定温度１９０（ダイス側）～２２０（ホッパー側）℃の条件にてペレット化し乳酸系樹脂組成物を得た。

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【００７７】
次いで、得られたペレット状の乳酸系樹脂組成物とポリメチルメタクリレート樹脂（アクリペットＶ、三菱レイヨン製）（耐熱温度（ＨＤＴ）＝９７℃（ＩＳＯ７５に準拠し荷重０．４５ＭＰａで測定））とを、樹脂温度が２２０℃に設定された２層Ｔ－ダイ製膜機（スクリュー径６５ｍｍφ、ダイス幅５００ｍｍ）のそれぞれ別のホッパーへ供給し、各層の厚みを、外層１（乳酸系樹脂組成物層）／外層２（ＰＭＭＡ層）＝７０／３０となるようにして、温度を３０℃に調整したキャストロール上に溶融樹脂を押出し、厚み１１００μｍの２層シートを得た。
【００７８】
得られた２層シートを、表面温度が１００℃になるように予熱した後、金型とプラグを用いて、真空圧空熱成形を行い成形体としてカップを得た。金型は、上部口径１００ｍｍ、底部口径６０ｍｍ、高さ１２０ｍｍ、絞り比１．２のカップ状の金型を用いた。
【００７９】
成形したカップの耐熱性および透明性を評価した。その結果を表１に示す。
【実施例３】
【００８０】
ポリ乳酸樹脂（ＬＡＣＥＡ（登録商標）：Ｈ－４００、三井化学（株）製）１００重量部と、エチレンビスステアリン酸アミド（アルフロー　Ｈ－５０Ｐ、日本油脂（株）製）０．５重量部とをヘンシェルミキサーにて混合後、押出機シリンダー設定温度１９０（ダイス側）～２２０（ホッパー側）℃の条件にてペレット化し乳酸系樹脂組成物を得た。
【００８１】
得られたペレット状の乳酸系樹脂組成物とポリメチルメタクリレート樹脂（アクリペットＶ、三菱レイヨン製）（耐熱温度（ＨＤＴ）＝９７℃（ＩＳＯ７５に準拠し荷重０．４５ＭＰａで測定））を、樹脂温度が２２０℃に設定された３層Ｔ－ダイ製膜機（スクリュー径６５ｍｍφ、ダイス幅５００ｍｍ）のそれぞれ別のホッパーへ供給し、各層の厚みを、外層１（ＰＭＭＡ層）／中間層（乳酸系樹脂組成物層）／外層２（ＰＭＭＡ層）＝２０／６０／２０となるようにして、温度を３０℃に調整したキャストロール上に溶融樹脂を押出し、厚み１１００μｍの３層シートを得た。
【００８２】
得られた３層シートを、表面温度が１００℃になるように予熱した後、金型とプラグを用いて、真空圧空熱成形を行い成形体としてカップを得た。金型は、上部口径１００ｍｍ、底部口径６０ｍｍ、高さ１２０ｍｍ、絞り比１．２のカップ状の金型を用いた。
【００８３】
成形したカップの耐熱性および透明性を評価した。その結果を表１に示す。
［比較例１］
ポリ乳酸樹脂（ＬＡＣＥＡ（登録商標）：Ｈ－４００、三井化学（株）製）１００重量部を、樹脂温度が２２０℃に設定された２層Ｔ－ダイ製膜機（スクリュー径６５ｍｍφ、ダイス幅５００ｍｍ）のホッパーへ供給し、温度を３０℃に調整したキャストロール上に溶融樹脂を押出し、厚み１１００μｍの２層シートを得た。
【００８４】
得られた２層シートを、表面温度が１００℃になるように予熱した後、金型とプラグを用いて、真空圧空熱成形を行い成形体としてカップを得た。金型は、上部口径１００ｍｍ、底部口径６０ｍｍ、高さ１２０ｍｍ、絞り比１．２のカップ状の金型を用いた。
【００８５】
成形したカップの耐熱性および透明性を評価した。その結果を表１に示す。
［比較例２］
ポリ乳酸樹脂（ＬＡＣＥＡ（登録商標）：Ｈ－４００、三井化学（株）製）１００重量部、エチレンビスステアリン酸アミド（アルフロー　Ｈ－５０Ｐ、日本油脂（株）製）０．５重量部をヘンシェルミキサーにて混合後、押出機シリンダー設定温度１９０（ダイス側）～２２０（ホッパー側）℃の条件にてペレット化し乳酸系樹脂組成物を得た。

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【００８６】
次いで、得られたペレット状の乳酸系樹脂組成物のみを、樹脂温度が２２０℃に設定された２層Ｔ－ダイ製膜機（スクリュー径６５ｍｍφ、ダイス幅５００ｍｍ）のホッパーへ供給し、温度を３０℃に調整したキャストロール上に溶融樹脂を押出し、厚み１１００μｍの２層シートを得た。
【００８７】
得られた２層シートを、表面温度が１００℃になるように予熱した後、金型とプラグを用いて、真空圧空熱成形を行い成形体としてカップを得た。金型は、上部口径１００ｍｍ、底部口径６０ｍｍ、高さ１２０ｍｍ、絞り比１．２のカップ状の金型を用いた。
【００８８】
成形したカップの耐熱性および透明性を評価した。その結果を表１に示す。
【００８９】
【表１】

表１

| | 実施例１ | 実施例２ | 実施例３ | 比較例１ | 比較例２ |
|---|---|---|---|---|---|
| 外層１ | ＰＬＡ | ＰＬＡ+<br>透明核剤 | ＰＭＭＡ | ＰＬＡ | ＰＬＡ+<br>透明核剤 |
| 中間層 | | | ＰＬＡ+<br>透明核剤 | | |
| 外層２ | ＰＭＭＡ | ＰＭＭＡ | ＰＭＭＡ | ＰＬＡ | ＰＬＡ+<br>透明核剤 |
| 寸法変化<br>65℃ | 2.0% | 1.1% | 1.0% | 形状保持困難 | 3.8% |
| 透明性 | 2% | 3% | 6% | 2% | 9% |
| 厚み | 250μm | 250μm | 250μm | 250μm | 250μm |

PLA:ポリ乳酸樹脂(LACEA(登録商標):H－400、三井化学(株)製)
透明核剤:エチレンビスステアリン酸アミド(アルフロー　H－50P、日本油脂(株)製)
PMMA:ポリメチルメタクリレート樹脂(アクリペットV、三菱レイヨン製)

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# PATENT ABSTRACTS OF JAPAN

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(54) **MOLDING**

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a molding more excellent in heat resistance than a conventional molding consisting of a polylactic acid composition.
SOLUTION: The molding is obtained by secondarily molding a multilayered sheet having at least one layer consisting a lactic acid type resin composition containing a lactic acid type polymer and at least one layer consisting of a heat-resistant thermoplastic resin composition containing a heat-resistant thermoplastic resin with a heat-resistant temperature (HDT) above 70° C (in conformity to ISO 75: load of 0.45 MPa) other than the lactic acid type polymer.



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权利要求书 1 页 说明书 5 页 附图 1 页

[54] 发明名称 完全生物降解聚乳酸涂层材料

[57] 摘要

一种完全生物降解聚乳酸涂层材料包含纸层和纸层上的增塑聚乳酸组合物涂层。所用增塑剂为选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂己二酸类聚酯和癸二酸类聚酯其中的一种或二种以上，增塑聚乳酸组合物，以重量百分比计算，内含有 100 份的聚乳酸，5～120 份复配增塑剂，0～1 份脂肪族酰胺爽滑剂，0～20 份无机填料。采用熔融挤出涂布方法或溶液涂布方法制备完全生物降解聚乳酸涂层纸。这种涂层纸具有防水、阻气、耐油脂、抗菌、彩色印刷、耐热、热封等功能。具有此种结构的涂层纸具有低成本性，便于工业化生产，并且具有完全生物降解特性，可以应用于制作纸杯、餐盒、一次性包装物等。

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1、一种完全生物降解聚乳酸涂层材料的制备方法，其特征在于涂层材料由纸层和纸层上的增塑聚乳酸组合物组成，纸层所用材料为由植物纤维制成的纸张、纸板或由聚乳酸纤维制成的无纺布。

2、如权利要求 1 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述增塑聚乳酸组合物以重量百分比计算，组合物内含有 100 份的聚乳酸，5～120 份复配增塑剂，0～1 份脂肪族酰胺爽滑剂，0～20 份无机填料。

3、如权利要求 1 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所用聚乳酸为结晶性聚乳酸或非结晶性聚乳酸。

4、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所用复配增塑剂选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂已二酸类聚酯和癸二酸类聚酯其中的一种或二种以上，用量相对于 100 重量份的聚乳酸为 5-120 重量份，优选为 20-80 重量份。

5、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述脂肪族酰胺爽滑剂为油酸酰胺或芥酸酰胺。

6、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述无机填料为二氧化硅、钛白粉、硅藻土、碳黑、碳酸钙或滑石粉。



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# 完全生物降解聚乳酸涂层材料

## 技术领域

本发明属于完全生物降解聚乳酸涂层材料的制备方法。

## 背景技术

基于石油化工产品的高分子材料以薄膜、片材、管材、纤维、泡沫体和其他形式在国防和民用领域得到广泛应用。这些高分子材料在使用后都成为废弃物而对自然环境造成一定影响。虽然世界各国对高分子废弃物的再生利用做了大量的研究和产业化努力，但收效并不理想，不能从根本上解决高分子废弃物对自然环境的污染问题。为了克服这一问题，世界各国对完全生物降解高分子材料给予越来越多的重视。

聚乳酸是一种完全生物降解的高分子材料，在自然环境中通过微生物产生的酶作用最终降解成无机物质如水和二氧化碳。在可降解的热塑性高分子材料中，聚乳酸具有最高的熔点，最高的玻璃化转变温度和力学强度，因此有较好的耐热性。但是，聚乳酸存在韧性差、加工温度范围较窄、原材料成本高等缺点，在要求柔软度的应用领域如软包装等领域中的应用受到限制。通过与增塑剂共混可以在很大程度上提高聚乳酸的韧性，尤其是有利于加工和降低成本。经过增塑的聚乳酸能用挤出，注塑，流延，吹塑，纺丝，双轴拉伸等多种方式进行加工。可以预期，这种完全生物降解聚乳酸涂层材料将在一次性包装物领域有广泛的应



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用。

中国专利 ZL 99125782.0， ZL 99252343.5 和 ZL 00263400.7 涉及纸塑复合结构的食品包装用复合材料，其外层为聚乳酸层或聚乳酸共聚物层。在这三项专利中未涉及增塑聚乳酸，因此其易加工性和低成本性受到限制。中国专利 ZL 00112783.7 涉及一种应用于医用防粘连膜的增塑聚乳酸材料，该材料中所用增塑剂包括水溶性增塑剂如聚乙二醇以及油溶性增塑剂如油酸、硬脂酸、癸酸、油酸乙酯。中国专利 ZL 02123145.1 涉及一种含有 5-50%重量份聚甘油乙酸酯增塑聚乳酸的可生物降解塑料产品。中国专利 ZL 03117482.5 涉及一种含有 2-15%医用增塑剂的聚乳酸组合物膜，所用增塑剂为聚乙二醇、柠檬酸三丁酯、乙酰柠檬酸三丁酯、寡聚乳酸。

发明内容

本发明的目的是提供一种完全生物降解聚乳酸涂层材料的制备方法。

由于无毒的可用于食品包装的多元醇酯类，柠檬酸酯类，聚酯类增塑剂对聚乳酸的增塑效果在耐热性、耐迁移性、相容性等方面各有优缺点，而单独使用效果不能令人满意。若采用包含两类或两类以上的复配增塑剂则会提高聚乳酸的综合使用性能，本发明是基于这一认识而获得的。

本发明中纸层所用材料由植物纤维制成的纸张或纸板或由聚乳酸纤维制成的无纺布，涂层所用材料为复配增塑剂与聚乳酸的组合物所用复配增塑剂选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三



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丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂已二酸类聚酯和癸二酸类聚酯期中的一种或二种以上，用量相对于 100 重量份的聚乳酸为 5-115 重量份，优选为 20-80 重量份；根据用途，聚乳酸组合物中可加入爽滑剂、无机填料，选用的爽滑剂为脂肪族酰胺、油酸酰胺或芥酸酰胺，其添加量相对于 100 重量份的聚乳酸为 0.05～1 份，选用的无机填料为二氧化硅、钛白粉、硅藻土、碳黑、碳酸钙或滑石粉，其添加量相对于 100 重量份的聚乳酸为 1～20 份；所用聚乳酸可以选用结晶性聚乳酸或非结晶性聚乳酸。

完全生物降解聚乳酸涂层材料的制备方法，采用熔融挤出涂布方法或溶液涂布方法实现，溶液涂布法包括转移涂布、浸涂、刮涂等常用涂布方法，其中溶剂选用丙酮、氯仿或两者的混合溶剂。

熔融挤出涂布的制备方法是首先将 100 重量份的聚乳酸与 5～120 份复配增塑剂按比例通过机械搅拌混合，经双螺杆挤出机熔融挤出造粒得到增塑聚乳酸后利用配有 T 型模头的挤出涂布设备将增塑聚乳酸挤出成膜状或片状压合于纸层上形成完全生物降解聚乳酸涂层材料；

溶液涂布的制备方法是首先将100重量份的聚乳酸与5～120份复配增塑剂以及 500～1000 重量份溶剂按比例搅拌混合均匀得到增塑聚乳酸溶液后，利用转移涂布、浸涂或刮涂，用涂布设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。

附图说明

附图 1 是完全生物降解聚乳酸涂层材料

图中（1）为纸层，（2）为涂层



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本发明结合附图 1 描述如下：完全生物降解聚乳酸涂层材料包含纸层（1）和纸层上的涂层（2）。具备这种结构的涂层纸便于工业化生产，并且具有完全生物降解特性，而且，这种涂层纸可以具有防水、阻气、耐油脂、抗菌、彩色印刷、耐热、热封等功能。具有此种结构的涂层纸可以应用于制作纸杯、餐盒、一次性包装物等。

具体实施方式

实施例 1：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，5 重量份复配增塑剂，0.1 重量份的油酸酰胺。复配增塑剂内含有 2 份聚乙二醇和 3 份柠檬酸三乙酯。将上述组成的聚乳酸、复配增塑剂和添加剂通过机械搅拌混合，经双螺杆挤出机熔融挤出造粒得到增塑聚乳酸组合物，利用配有 T 型模头的挤出涂布设备将增塑聚乳酸组合物挤出成膜状或片状压合于纸层上形成完全生物降解聚乳酸涂层材料。

实施例 2：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，30 重量份复配增塑剂。复配增塑剂内含有 20 份甘油三乙酸酯和 10 份聚癸二酸 1、3-丁二醇酯，材料的制备方法同实施例 1。

实施例 3：

涂层材料的组成中包含 100 重量份的结晶性聚乳酸，70 重量份复配增塑剂， 5 重量份硅藻土。复配增塑剂的内含有 20 份甘油三乙酸酯，20 份聚己二酸 1，3-丁二醇酯和 30 份乙酰柠檬酸三乙酯，材料的制备方法同实施例 1。



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实施例 4：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，120 重量份复配增塑剂，0.5 重量份的油酸酰胺，20 重量份碳酸钙。复配增塑剂的组成内含有 40 份甘油三乙酸酯，60 份聚癸二酸 1、3-丁二醇酯和 20 份乙酰柠檬酸三丁酯，材料的制备方法同实施例 1。

实施例 5：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，60 重量份复配增塑剂，0.1 重量份的油酸酰胺，3 重量份钛白粉。复配增塑剂的组成内含有 20 份柠檬酸三丁酯和 40 份聚已二酸丙二醇酯，采用 800 重量份的氯仿为溶剂与聚乳酸和增塑剂搅拌混合均匀得到增塑聚乳酸溶液后，利用转移涂布设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。

实施例 6：

涂层材料的组成中包含 100 重量份的结晶性聚乳酸，100 重量份复配增塑剂，0.2 重量份的油酸酰胺，1 重量份滑石粉。复配增塑剂的组成内含有 40 份甘油三乙酸酯，30 份乙酰柠檬酸三丁酯和 30 份聚己二酸 1，3-丁二醇酯，采用 500 重量份的氯仿和 100 重量份的丙酮为溶剂与聚乳酸和增塑剂搅拌混合均匀得到增塑聚乳酸溶液后，利用刮涂设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。



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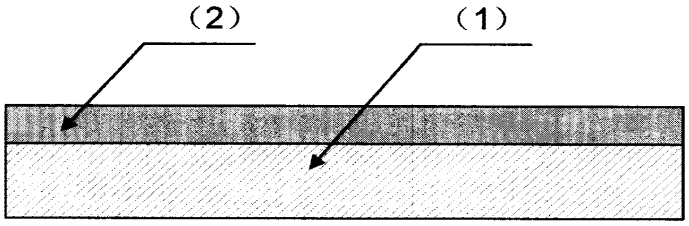



图 1



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权利要求书 1 页 说明书 5 页 附图 1 页

[54] 发明名称 完全生物降解聚乳酸涂层材料

[57] 摘要

一种完全生物降解聚乳酸涂层材料包含纸层和纸层上的增塑聚乳酸组合物涂层。所用增塑剂为选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂己二酸类聚酯和癸二酸类聚酯其中的一种或二种以上，增塑聚乳酸组合物，以重量百分比计算，内含有 100 份的聚乳酸，5～120 份复配增塑剂，0～1 份脂肪族酰胺爽滑剂，0～20 份无机填料。采用熔融挤出涂布方法或溶液涂布方法制备完全生物降解聚乳酸涂层纸。这种涂层纸具有防水、阻气、耐油脂、抗菌、彩色印刷、耐热、热封等功能。具有此种结构的涂层纸具有低成本性，便于工业化生产，并且具有完全生物降解特性，可以应用于制作纸杯、餐盒、一次性包装物等。

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1、一种完全生物降解聚乳酸涂层材料的制备方法，其特征在于涂层材料由纸层和纸层上的增塑聚乳酸组合物组成，纸层所用材料为由植物纤维制成的纸张、纸板或由聚乳酸纤维制成的无纺布。

2、如权利要求 1 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述增塑聚乳酸组合物以重量百分比计算，组合物内含有 100 份的聚乳酸，5～120 份复配增塑剂，0～1 份脂肪族酰胺爽滑剂，0～20 份无机填料。

3、如权利要求 1 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所用聚乳酸为结晶性聚乳酸或非结晶性聚乳酸。

4、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所用复配增塑剂选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂已二酸类聚酯和癸二酸类聚酯其中的一种或二种以上，用量相对于 100 重量份的聚乳酸为 5-120 重量份，优选为 20-80 重量份。

5、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述脂肪族酰胺爽滑剂为油酸酰胺或芥酸酰胺。

6、权利要求 1 和 2 所述的完全生物降解聚乳酸涂层材料的制备方法，其特征在于所述无机填料为二氧化硅、钛白粉、硅藻土、碳黑、碳酸钙或滑石粉。



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# 完全生物降解聚乳酸涂层材料

## 技术领域

本发明属于完全生物降解聚乳酸涂层材料的制备方法。

## 背景技术

基于石油化工产品的高分子材料以薄膜、片材、管材、纤维、泡沫体和其他形式在国防和民用领域得到广泛应用。这些高分子材料在使用后都成为废弃物而对自然环境造成一定影响。虽然世界各国对高分子废弃物的再生利用做了大量的研究和产业化努力，但收效并不理想，不能从根本上解决高分子废弃物对自然环境的污染问题。为了克服这一问题，世界各国对完全生物降解高分子材料给予越来越多的重视。

聚乳酸是一种完全生物降解的高分子材料，在自然环境中通过微生物产生的酶作用最终降解成无机物质如水和二氧化碳。在可降解的热塑性高分子材料中，聚乳酸具有最高的熔点，最高的玻璃化转变温度和力学强度，因此有较好的耐热性。但是，聚乳酸存在韧性差、加工温度范围较窄、原材料成本高等缺点，在要求柔软度的应用领域如软包装等领域中的应用受到限制。通过与增塑剂共混可以在很大程度上提高聚乳酸的韧性，尤其是有利于加工和降低成本。经过增塑的聚乳酸能用挤出，注塑，流延，吹塑，纺丝，双轴拉伸等多种方式进行加工。可以预期，这种完全生物降解聚乳酸涂层材料将在一次性包装物领域有广泛的应



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用。

中国专利 ZL 99125782.0， ZL 99252343.5 和 ZL 00263400.7 涉及纸塑复合结构的食品包装用复合材料，其外层为聚乳酸层或聚乳酸共聚物层。在这三项专利中未涉及增塑聚乳酸，因此其易加工性和低成本性受到限制。中国专利 ZL 00112783.7 涉及一种应用于医用防粘连膜的增塑聚乳酸材料，该材料中所用增塑剂包括水溶性增塑剂如聚乙二醇以及油溶性增塑剂如油酸、硬脂酸、癸酸、油酸乙酯。中国专利 ZL 02123145.1 涉及一种含有 5-50%重量份聚甘油乙酸酯增塑聚乳酸的可生物降解塑料产品。中国专利 ZL 03117482.5 涉及一种含有 2-15%医用增塑剂的聚乳酸组合物膜，所用增塑剂为聚乙二醇、柠檬酸三丁酯、乙酰柠檬酸三丁酯、寡聚乳酸。

发明内容

本发明的目的是提供一种完全生物降解聚乳酸涂层材料的制备方法。

由于无毒的可用于食品包装的多元醇酯类，柠檬酸酯类，聚酯类增塑剂对聚乳酸的增塑效果在耐热性、耐迁移性、相容性等方面各有优缺点，而单独使用效果不能令人满意。若采用包含两类或两类以上的复配增塑剂则会提高聚乳酸的综合使用性能，本发明是基于这一认识而获得的。

本发明中纸层所用材料由植物纤维制成的纸张或纸板或由聚乳酸纤维制成的无纺布，涂层所用材料为复配增塑剂与聚乳酸的组合物所用复配增塑剂选自聚乙二醇、甘油三乙酸酯，柠檬酸三乙酯，柠檬酸三



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丁酯，乙酰柠檬酸三乙酯，乙酰柠檬酸三丁酯或聚酯类增塑剂已二酸类聚酯和癸二酸类聚酯期中的一种或二种以上，用量相对于 100 重量份的聚乳酸为 5-115 重量份，优选为 20-80 重量份；根据用途，聚乳酸组合物中可加入爽滑剂、无机填料，选用的爽滑剂为脂肪族酰胺、油酸酰胺或芥酸酰胺，其添加量相对于 100 重量份的聚乳酸为 0.05～1 份，选用的无机填料为二氧化硅、钛白粉、硅藻土、碳黑、碳酸钙或滑石粉，其添加量相对于 100 重量份的聚乳酸为 1～20 份；所用聚乳酸可以选用结晶性聚乳酸或非结晶性聚乳酸。

完全生物降解聚乳酸涂层材料的制备方法，采用熔融挤出涂布方法或溶液涂布方法实现，溶液涂布法包括转移涂布、浸涂、刮涂等常用涂布方法，其中溶剂选用丙酮、氯仿或两者的混合溶剂。

熔融挤出涂布的制备方法是首先将 100 重量份的聚乳酸与 5～120 份复配增塑剂按比例通过机械搅拌混合，经双螺杆挤出机熔融挤出造粒得到增塑聚乳酸后利用配有 T 型模头的挤出涂布设备将增塑聚乳酸挤出成膜状或片状压合于纸层上形成完全生物降解聚乳酸涂层材料；

溶液涂布的制备方法是首先将100重量份的聚乳酸与5～120份复配增塑剂以及 500～1000 重量份溶剂按比例搅拌混合均匀得到增塑聚乳酸溶液后，利用转移涂布、浸涂或刮涂，用涂布设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。

附图说明

附图 1 是完全生物降解聚乳酸涂层材料

图中（1）为纸层，（2）为涂层



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本发明结合附图 1 描述如下：完全生物降解聚乳酸涂层材料包含纸层（1）和纸层上的涂层（2）。具备这种结构的涂层纸便于工业化生产，并且具有完全生物降解特性，而且，这种涂层纸可以具有防水、阻气、耐油脂、抗菌、彩色印刷、耐热、热封等功能。具有此种结构的涂层纸可以应用于制作纸杯、餐盒、一次性包装物等。

具体实施方式

实施例 1：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，5 重量份复配增塑剂，0.1 重量份的油酸酰胺。复配增塑剂内含有 2 份聚乙二醇和 3 份柠檬酸三乙酯。将上述组成的聚乳酸、复配增塑剂和添加剂通过机械搅拌混合，经双螺杆挤出机熔融挤出造粒得到增塑聚乳酸组合物，利用配有 T 型模头的挤出涂布设备将增塑聚乳酸组合物挤出成膜状或片状压合于纸层上形成完全生物降解聚乳酸涂层材料。

实施例 2：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，30 重量份复配增塑剂。复配增塑剂内含有 20 份甘油三乙酸酯和 10 份聚癸二酸 1、3-丁二醇酯，材料的制备方法同实施例 1。

实施例 3：

涂层材料的组成中包含 100 重量份的结晶性聚乳酸，70 重量份复配增塑剂， 5 重量份硅藻土。复配增塑剂的内含有 20 份甘油三乙酸酯，20 份聚己二酸 1，3-丁二醇酯和 30 份乙酰柠檬酸三乙酯，材料的制备方法同实施例 1。



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实施例 4：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，120 重量份复配增塑剂，0.5 重量份的油酸酰胺，20 重量份碳酸钙。复配增塑剂的组成内含有 40 份甘油三乙酸酯，60 份聚癸二酸 1、3-丁二醇酯和 20 份乙酰柠檬酸三丁酯，材料的制备方法同实施例 1。

实施例 5：

涂层材料的组成中包含 100 重量份的非结晶性聚乳酸，60 重量份复配增塑剂，0.1 重量份的油酸酰胺，3 重量份钛白粉。复配增塑剂的组成内含有 20 份柠檬酸三丁酯和 40 份聚已二酸丙二醇酯，采用 800 重量份的氯仿为溶剂与聚乳酸和增塑剂搅拌混合均匀得到增塑聚乳酸溶液后，利用转移涂布设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。

实施例 6：

涂层材料的组成中包含 100 重量份的结晶性聚乳酸，100 重量份复配增塑剂，0.2 重量份的油酸酰胺，1 重量份滑石粉。复配增塑剂的组成内含有 40 份甘油三乙酸酯，30 份乙酰柠檬酸三丁酯和 30 份聚己二酸 1，3-丁二醇酯，采用 500 重量份的氯仿和 100 重量份的丙酮为溶剂与聚乳酸和增塑剂搅拌混合均匀得到增塑聚乳酸溶液后，利用刮涂设备将增塑聚乳酸以膜或片状形式涂布于纸层上，烘干溶剂形成完全生物降解聚乳酸涂层材料。



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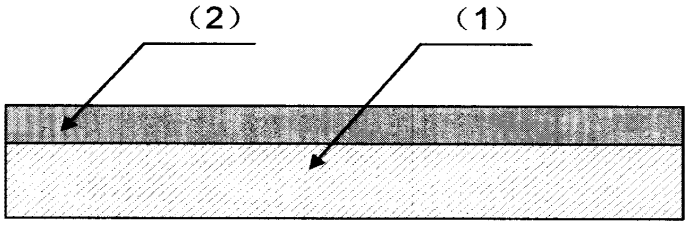



图 1



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[19]中华人民共和国国家知识产权局

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# [12]实用新型专利说明书

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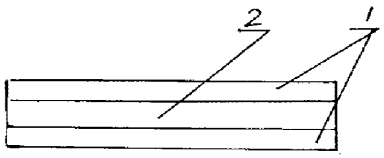
代理人 王淑勤 周建观

权利要求书 1 页 说明书 1 页 附图页数 1 页

[54]实用新型名称 纸与降解淋膜的复合材料

[57]摘要

一种纸与降解淋膜的复合材料，它是在基纸上淋上降解淋膜层，它具有投资少，价格便宜，易降解，不造成白色污染，并且卫生，保暖性好等优点。




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# 权 利 要 求 书

1、一种纸与降解淋膜的复合材料，其特征在于：在基纸(2)的面上淋上降解淋膜层(1)。

2、根据权利要求1所述的复合材料，其特征在于：在基纸(2)的一面或两面淋上降解淋膜层(1)。

# 说　明　书

## 纸与降解淋膜复合材料

本实用新型涉及一种适用于制作餐饮具的复合材料。

目前，制作餐饮具的材料，特别是一次性快餐饮具大多采用聚苯乙烯泡沫塑料制作，但是，由泡沫塑料制作的一次性餐饮具使用丢弃后不会自然降解，污染环境，造成白色污染，并且在高温下会产生二恶英致癌物，现国家已开始禁止使用，为至市场相继开发可降解塑料泡沫餐具，其缺点成本高，与原产品不易区分，使消费者和环保部门无法支持；纸浆模餐具因耐温低只适合凉干食品；谷糠、柑桔纤维餐具易碎，难以制作连体带盖饭盖，外观色彩难以改观。

本实用新型的目的是提供一种能自然解降，不造成白色污染的餐饮具材料。

实现本实用新型目的的技术方案是；在基纸的面上淋上降解淋膜层，降解淋膜层可以在基纸的一个面或者两个面上。

由于本实用新型的组成材料是由纸及降解淋膜组成，这些材质在自然界中2～12个月内可以降解，故不会造成白色污染。

下面结合附图和实施例对本实用新型作进一步说明。

图1，基纸的两面为降解淋膜层的结构示意图。

图2，基纸的一面为降解淋膜层的结构示意图。

在基纸（2）上用塑料挤出机加热降解淋膜原料熔化成淋状直接淋在基纸（2）一面上形成降淋膜层（1）参见图2，制成基纸一面为降解淋膜层的复合材料，也可以直接淋在基纸（2）的两个面上形成降解淋膜层（1）参见图1，制成基纸两面为降解淋膜层的复合材料。基纸（2）可以采用通常所用的纸与纸板等材料，降解淋膜层材料可由低密度聚乙烯或者聚丙烯与复合降解树脂（牌号为强力1号、北京塑料研究中心生产）所制成。

本实用新型具有以下优点：首先是基纸原料广、价格便宜，制成产品的成本低；其次是极薄的降解淋膜层，淋膜厚度为0.015mm左右，易降解，不造成白色污染，而且光亮、无毒、卫生、美观、防水、防油、耐热、保暖性能好；另外，生产工艺简单，投资少。

# 说 明 书 附 图

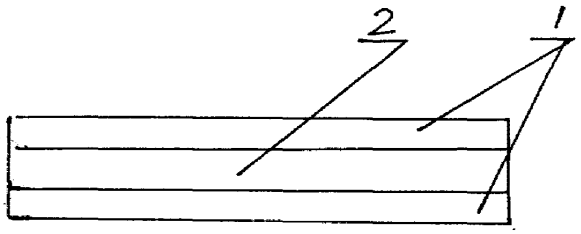



图 1

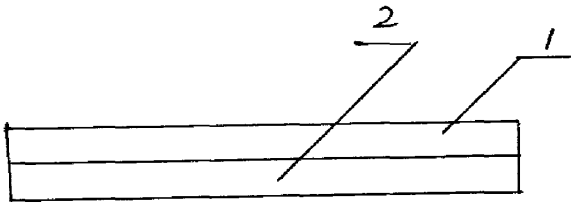



图 2

[19]中华人民共和国国家知识产权局

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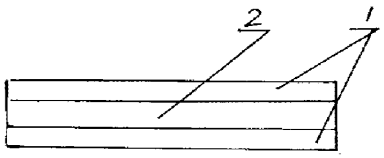
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权利要求书 1 页 说明书 1 页 附图页数 1 页

[54]实用新型名称 纸与降解淋膜的复合材料

[57]摘要

一种纸与降解淋膜的复合材料，它是在基纸上淋上降解淋膜层，它具有投资少，价格便宜，易降解，不造成白色污染，并且卫生，保暖性好等优点。




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# 权 利 要 求 书

1、一种纸与降解淋膜的复合材料，其特征在于：在基纸(2)的面上淋上降解淋膜层(1)。

2、根据权利要求1所述的复合材料，其特征在于：在基纸(2)的一面或两面淋上降解淋膜层(1)。

# 说　明　书

## 纸与降解淋膜复合材料

本实用新型涉及一种适用于制作餐饮具的复合材料。

目前，制作餐饮具的材料，特别是一次性快餐饮具大多采用聚苯乙烯泡沫塑料制作，但是，由泡沫塑料制作的一次性餐饮具使用丢弃后不会自然降解，污染环境，造成白色污染，并且在高温下会产生二恶英致癌物，现国家已开始禁止使用，为至市场相继开发可降解塑料泡沫餐具，其缺点成本高，与原产品不易区分，使消费者和环保部门无法支持；纸浆模餐具因耐温低只适合凉干食品；谷糠、柑桔纤维餐具易碎，难以制作连体带盖饭盖，外观色彩难以改观。

本实用新型的目的是提供一种能自然解降，不造成白色污染的餐饮具材料。

实现本实用新型目的的技术方案是；在基纸的面上淋上降解淋膜层，降解淋膜层可以在基纸的一个面或者两个面上。

由于本实用新型的组成材料是由纸及降解淋膜组成，这些材质在自然界中2～12个月内可以降解，故不会造成白色污染。

下面结合附图和实施例对本实用新型作进一步说明。

图1，基纸的两面为降解淋膜层的结构示意图。

图2，基纸的一面为降解淋膜层的结构示意图。

在基纸（2）上用塑料挤出机加热降解淋膜原料熔化成淋状直接淋在基纸（2）一面上形成降淋膜层（1）参见图2，制成基纸一面为降解淋膜层的复合材料，也可以直接淋在基纸（2）的两个面上形成降解淋膜层（1）参见图1，制成基纸两面为降解淋膜层的复合材料。基纸（2）可以采用通常所用的纸与纸板等材料，降解淋膜层材料可由低密度聚乙烯或者聚丙烯与复合降解树脂（牌号为强力1号、北京塑料研究中心生产）所制成。

本实用新型具有以下优点：首先是基纸原料广、价格便宜，制成产品的成本低；其次是极薄的降解淋膜层，淋膜厚度为0.015mm左右，易降解，不造成白色污染，而且光亮、无毒、卫生、美观、防水、防油、耐热、保暖性能好；另外，生产工艺简单，投资少。

# 说 明 书 附 图

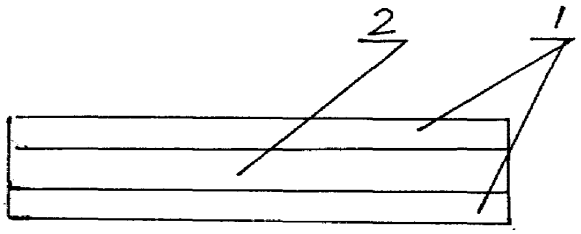



图 1

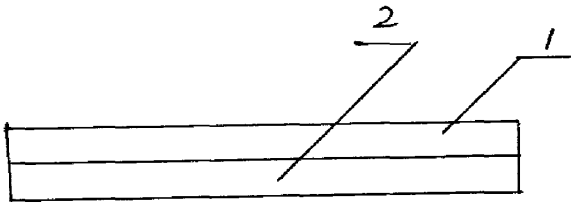



图 2

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(54) Title: FIBROUS SHEETS COATED OR IMPREGNATED WITH BIODEGRADABLE POLYMERS OR POLYMERS BLENDS

(57) Abstract: Fibrous sheets are coated or impregnated with a biodegradable composition to render the sheets more resistant to penetration by liquids. Biodegradable polymer blends suitable for use in coating or impregnating a fibrous sheet can be manufactured from at least one "hard" biodegradable polymer and at least one "soft" biodegradable polymer. "Hard" biopolymers typically have a glass transition temperature of at least about 10°C. "Soft" biodegradable polymers typically have a glass transition temperature less than about 0°C. Another useful biodegradable polymer composition includes one or more biodegradable polymers and sufficient inorganic filler so as to render the treated sheet microwaveable. The biodegradable polymer compositions are especially well-suited for coating or impregnating paper sheets, e.g., 12-15 lb/3000 $ft^2$ tissue paper to yield food wraps. Food wraps will typically be manufactured to have good "dead-fold" properties so as to remain in a wrapped position and not spring back to an "unwrapped" form.

# FIBROUS SHEETS COATED OR IMPREGNATED WITH BIODEGRADABLE POLYMERS OR POLYMERS BLENDS

## BACKGROUND OF THE INVENTION

### 1. The Field of the Invention

The present invention relates generally to biodegradable polymers or polymer blends and sheets manufactured therefrom. More particularly, the present invention relates to fibrous sheets that are coated or impregnated with biodegradable polymers or blends that render the sheets more resistant to liquids. The resulting sheets are suitable for a number of applications, such as disposable wraps, bags, pouches or other packaging materials.

### 2. The Relevant Technology

As affluence grows, so does the ability to purchase and accumulate more things. Never before in the history of the world has there been such a large number of people with such tremendous buying power. The ability to purchase relatively inexpensive goods, such as books, tools, toys and food, is a luxury enjoyed by virtually all levels of society, even those considered to be at the poorer end of the spectrum. Because a large percentage of what is purchased is prepackaged, there has been a tremendous increase in the amount of disposable packaging materials that are routinely discarded into the environment as solid waste. Thus, as society becomes more affluent, it generates more disposable trash.

Some packaging materials are only intended for a single use, such as boxes, cartons, pouches, bags and wraps used to package items purchased from wholesale and retail outlets. Even the advent of computers and "paperless" transactions has not stemmed the rising tide of packaging wastes. Indeed, the onset of "e-commerce" has spawned a great mail-order fad, thus creating a whole new market of individually packaged and shipped items.

Moreover, the modern, fast-paced lifestyle has greatly disrupted traditional eating routines in which people prepared their own meals and sat down as a family or group. Instead, people grab food on the run, thus creating ever-increasing amounts of fast-food packaging materials that are used once and then discarded. In view of the high volume of disposable packaging materials being generated, some countries, particularly those in Europe, have mandated either the recycling of fast food generated wastes or the use of

packaging materials which are "biodegradable" or "compostable". Environmental activists commonly pressure companies that generate solid waste to find more environmentally friendly alternatives. There is therefore an ever-present need to develop biodegradable alternatives to nonbiodegradable packaging materials.

Paper, paperboard and other fibrous sheets made from natural cellulose-based fibers are biodegradable. However, fibrous sheets tend to be porous. As a result, they do not provide good barriers against water, oil or other liquids. When fibrous sheets are used in applications where they will be exposed to liquids, they must generally be treated with a liquid-resistant material, such as paraffin wax or plastic. By doing so, however, the fibrous sheets are no longer biodegradable, but are as resistant to degradation as plastic or paraffin wax.

In view of the foregoing, it would be an advancement in the art to provide fibrous sheets that were resistant to liquids and that were biodegradable. In addition or alternatively, it would be a further advancement in the packaging art to provide improved fibrous sheets that were not only resistant to liquids, but still had good breathability and water vapor transmission compared to conventional fibrous sheets treated with wax or plastic.

## SUMMARY OF THE INVENTION

The invention encompasses fibrous sheets that are coated or impregnated with biodegradable polymers or polymer blends in order to yield sheets that are more resistant to liquids (generally "treated sheets" or "treated fibrous sheets"). The treated sheets can be used to manufacture a wide variety of articles of manufacture, including packaging materials, such as wraps, bags, pouches, cartons, jugs, cups, plates, bowls, trays, platters, lids, straws, and the like.

Exemplary fibrous sheets that may be treated with biodegradable polymers include, but are not limited to, tissue papers, paper sheets, felts, paperboard, wovens and nonwovens. In one aspect of the invention, fibrous sheets are coated or impregnated with a biodegradable polymer blend comprising at least one thermoplastic biodegradable polymer having relatively high stiffness and at least one thermoplastic biodegradable polymer having relatively high flexibility. Thus, the present invention provides blends that possess or demonstrate surprising synergistic effects that are particularly well-suited by use in treating fibrous sheets.

For example, blends containing a relatively stiff BIOMAX polymer, a modified polyethylene terephthalate (PET) sold by DuPont, and a relatively soft or flexible

polymer ECOFLEX, an aliphatic-aromatic copolymer sold by BASF, and/or EASTAR BIO, an aliphatic-aromatic copolymer sold by Eastman Chemical, have been shown to have strength and elongation properties which are superior to either biopolymer taken alone. Other stiff biopolymers include BAK, a polyesteramide sold by Bayer, and polylactic acid (PLA).

BIOMAX is characterized as having a relatively high glass transition temperature and is highly crystalline at room temperature. BIOMAX tends to be quite stiff or brittle when formed into films or sheets. It also has poor elongation or elasticity. ECOFLEX and EASTAR BIO, on the other hand, are characterized as having relatively low glass transition temperatures and are relatively amorphous or noncrystalline at room temperature, all of which contribute to the high softness, elasticity and high elongation. Even so, various blends of BIOMAX and ECOFLEX and/or EASTAR BIO actually exhibit higher elongation than ECOFLEX by itself, as well as higher break stress compared to either BIOMAX or ECOFLEX by themselves.

Other polymer blends that can be used to treat fibrous sheets include, but are not limited to, a blend of ECOFLEX, PLA and thermoplastic starch (TPS) and a blend of BAK (a polyesteramide manufactured by Bayer Corporation) and TPS. In each case, blending a biopolymer having a relatively low glass transition temperature with a biopolymer having a relatively high glass transition temperature results in a polymer blend that exhibits the desired characteristics of each polymer by itself. In some cases, the blends exhibit better properties, while diminishing or minimizing the negative properties of each biopolymer by itself.

In general, biodegradable polymers that may be characterized as being relatively "stiff" or less flexible include polymers that have a glass transition temperature of at least about 10°C. Conversely, biodegradable polymers that may be characterized as being relatively "soft" include polymers that have a glass transition temperature less than about 0°C. "Stiff" biodegradable polymers preferably have a glass transition temperature of at least about 15°C., more preferably at least about 25°C., and most preferably at least about 35°C. "Soft" biodegradable polymers preferably have a glass transition temperature of less than about –4°C., more preferably less than about –10°C., more especially preferably less than about –20°C., and most preferably less than about –30°C. In addition, "stiff" polymers tend to be more crystalline; while "soft" polymers are generally less crystalline and more amorphous, particularly at room temperature.

When a blend of soft and stiff biodegradable polymers is used to coat or impregnate a fibrous sheet, the relatively stiff biodegradable polymer may have a concentration in a range of about 20% to about 99% by weight of the blend of biodegradable polymers exclusive of the fibrous sheet and any fillers. The stiff biodegradable polymer preferably has a concentration of at least about 30% by weight of the polymer blend, more preferably at least about 40% by weight of the polymer blend, more especially preferably greater than, but not including, 50% by weight of the polymer blend, and most preferably greater than about 55% by weight of the polymer blend.

When a blend of soft and stiff biodegradable polymers is used to coat or impregnate a fibrous sheet, the relatively soft biodegradable polymer may have a concentration in a range of about 1% to about 80% by weight of the blend of biodegradable polymers. The soft biodegradable polymer preferably has a concentration up to about 70% by weight of the polymer blend, more preferably up to about 60% by weight of the polymer blend, more especially preferably less than, but not including, 50% by weight of the polymer blend, and most preferably up to about 45% by weight of the polymer blend.

Biodegradable polymers used to treat fibrous sheets within the scope of the present invention include, but are not limited to, synthetic polyesters, semi-synthetic polyesters made by fermentation (*e.g.*, PHB and PHBV), polyesteramides, polycarbonates, and polyester urethanes. It is also within the scope of the invention to optionally include a variety of natural polymers and their derivatives, such as polymers comprising or derived from starch, cellulose, other polysaccharides and proteins. A single biodegradable polymer blended with an inorganic filler (*e.g.*, silica or calcium carbonate) may also be used to treat a fibrous sheet in order to yield a treated sheet that is more heat resistant.

It is within the scope of the invention to incorporate inorganic and organic fillers in order to decrease self-adhesion, lower the cost, and increase the modulus of elasticity (Young's modulus) of biodegradable polymers used to treat fibrous sheets as well as the resulting sheets. Examples of inorganic fillers include calcium carbonate, titanium dioxide, silica, aluminum oxide, talc, mica, and the like. Examples of organic fillers include wood flour, ground seeds, cellulose particles, polymeric particles, ungelatinized starch granules, and the like. In addition, plasticizers may be used to impart desired softening and elongation properties.

In the case of fibrous sheets intended to be used as "wraps", such as wraps used to enclose meats, other perishable food items, and especially fast food items (*e.g.*, sandwiches, burgers and dessert items), it may be desirable to provide wraps having good "dead-fold" properties so that once folded, wrapped or otherwise manipulated into a desired orientation, such wraps will tend to substantially maintain their orientation so as to not spontaneously unfold or unwrap, as occurs with a large number of plastic sheets and films (*e.g.*, polyethylene). Dead-fold is a measure of the ability of a sheet or film to retain a crease, crinkle or other bend. It is measured independently of self cling, heat sealing, or the use of an adhesive to maintain a desired orientation.

Whereas the fibrous sheets themselves may impart or inherently possess dead-fold properties, polymers and polymer blends used to treat fibrous sheets may be engineered so as to have a relatively high Young's modulus, preferably at least about 100 MPa, more preferably at least about 150 MPa, and most preferably at least about 200 MPa. In general, increasing the concentration of the stiff biopolymer will tend to increase the Young's modulus and the resulting dead-fold properties. It should be understood, however, that Young's modulus only loosely correlates to dead-fold and does not, in every case, serve to define or predict the dead-fold properties of a sheet or film formed from a polymer or polymer blend.

Including particulate fillers within the polymer or polymer blend used to coat or impregnate a fibrous sheet is another way to increase dead-fold of the resulting sheet. When used to increase dead-fold, particulate fillers are typically included in an amount of at least about 5% by weight of the polymer or polymer blend, preferably at least about 10% by weight, more preferably at least about 15% by weight, more especially preferably at least about 20% by weight, and most preferably at least about 30% by weight of the polymer or polymer blend used to treat a fibrous sheet.

Yet another way to increase dead-fold is to increase the surface area, or "bulk hand feel", of treated sheets according to the invention. This may be accomplished, for example, by disrupting the generally smooth, planar nature of the treated sheet, *e.g.*, by embossing, crimping, quilting or otherwise texturing the sheet so as to have regularly spaced-apart or random hills and valleys rather than simply being a perfectly smooth, planar sheet. A treated sheet may be textured, for example, by passing the sheet through a pair of knurled or other embossing-type rollers. Such texturing increases the ability of a treated sheet to take and maintain a fold, thus improving the dead-fold properties of the sheet.

The surface area of a treated sheet may also be increased by incorporating particulate fillers within the polymer or polymer blend used to coat or impregnate the fibrous sheet in order form surface irregularities within the surface of the treated sheet. This may be accomplished, for example, by incorporating filler particles, at least a portion of which, have a particle size diameter equal to or greater than the thickness of the polymer or polymer blend one or both sides of the treated sheet.

When used to wrap foods, or whenever good dead-fold properties are desired, treated sheets according to the invention can be engineered so as to have a dead-fold of at least about 50% (*i.e.*, when creased using a standard dead-fold test, the sheets and films will maintain at least about 50% of their original crease). Preferably, the treated sheets will have a dead-fold of at least about 60%, more preferably at least about 70%, more especially preferably at least about 80%, and most especially preferably at least about 90%. Treated fibrous sheets according to the invention can have dead-fold approaching or equal to 100% (*i.e.*, when folded such sheets remain folded absent the application of an external force sufficient to reverse the fold). By way of comparison, sheets and films made from polyethylene (*e.g.*, for use in making sandwich or garbage bags) typically have a dead-fold of 0%.

In some cases, it may be desirable for treated sheets according to the invention to "breath". As set forth above, particulate fillers, both organic and inorganic, can be used to increase the modulus of elasticity and/or dead-fold. Such fillers can also advantageously create "cavitation" whenever sheets or films used to coat or impregnate fibrous sheets are stretched during processing. Cavitation occurs as the thermoplastic polymer fraction is pulled in either a monoaxial or biaxial direction and the filler particles create a discontinuity in the film or sheet that increases in size during stretching. In essence, a portion of the stretched polymer pulls away from the filler particles, resulting in tiny cavities in the vicinity of the filler particles. This, in turn, results in greatly increased breathability and vapor transmission of the sheets and films. The ability of inorganic filler particles to create cavitation increases as the particle size diameter approaches or exceeds the thickness of the polymer or polymer blend.

Another advantage of utilizing biodegradable polymers to treat fibrous sheets is that biopolymers are generally able to accept and retain print much more easily than conventional plastics or waxes used to treat papers. Many plastics and waxes are highly hydrophobic and must be surface oxidized in order to provide a chemically receptive surface to which ink can adhere. Biodegradable polymers, on the other hand, typically

include a significant fraction of oxygen-containing moieties, such as ester, amide and/or urethane groups, to which inks can more readily adhere.

The treated sheets according to the invention may comprise single or multiple layers as desired. The fibrous sheets can be impregnated or coated on one or both sides, or any portion thereof. Multiple fibrous sheets can be joined or sandwiched together with one or more layers of biodegradable polymers, and optionally one or more auxiliary sheets (*e.g.*, metals foils). Fibrous sheets may be coated or impregnated by film blowing, co-extrusion, casting, and coating techniques known in the art. In one embodiment, a thermoplastic biodegradable composition is heated to a molten state and then spread over a fibrous sheet using a doctor blade. In another embodiment, the thermoplastic biodegradable composition is sprayed onto the fibrous sheet. Thermoplastic biodegradable polymers used to treat fibrous sheets result in treated sheets that can be heat sealed to join two ends together to form sacks, pockets, pouches, and the like. They can be laminated onto existing sheets or substrates.

Notwithstanding the advantages of using biodegradable polymers and polymer blends compared to polyethylene or other non-biodegradable polymers, biodegradable polymers tend to have a much lower melt flow index (MFI) compared to non-biodegradable polymers such as polyethylene, which makes biodegradable polymers more difficult to spread or spray onto a fibrous sheet. It may therefore be advantageous to incorporate one or more of water, solvent, or plasticizer, and/or increase the temperature of the biodegradable polymer or polymer blend well above its softening temperature or range, but without burning or otherwise harming it, to increase its MFI so as to facilitate the coating or impregnating process.

In one preferred embodiment, 4-5 lb/1000 $ft^2$ (12-15 lb/3000 $ft^2$) tissue paper is treated with a biodegradable polymer blend to render it more resistant to penetration by liquids. Of course, it is certainly within the scope of the invention to utilize any weight paper or tissue paper, *e.g.*, tissue paper ranging in weight from 8 lb/3000 $ft^2$ up to 60 lb/3000 $ft^2$. One of the benefits of coating or impregnating a fibrous sheet with a biodegradable polymer or polymer blend, as compared to simply making a sheet or film from the polymer blend itself, is that the fibrous sheet core increases the thermal stability of the resulting article of manufacture. This is beneficial in the case of wraps because increasing the thermal stability increases their ability to be microwaved without degrading or melting onto the food that is wrapped therein.

Increasing the amount of inorganic fillers within the biodegradable polymer or polymer blend used to coat or impregnate a fibrous sheet also increases the microwaveability of the resulting wraps. Providing biodegradable polymer wraps that are microwaveable is an improvement over wraps made using polyethylene, which are neither biodegradable nor microwave safe.

These and other advantages and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

## BRIEF DESCRIPTION OF THE DRAWINGS

In order that the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention briefly described above will be rendered by reference to a specific embodiment thereof which is illustrated in the appended drawings. Understanding that these drawings depict only a typical embodiment of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings, in which:

Figure 1 is a plot of the percent elongation at break versus the applied strain rate for various neat and blended polymer films;

Figure 2 is a plot of the percent elongation of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 500 mm/min.;

Figure 3 is a plot of the percent elongation of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 1000 mm/min.;

Figure 4 is a plot of the break stress versus the applied strain rate for various neat and blended polymer films;

Figure 5 is a plot of the break stress of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 500 mm/min.;

Figure 6 is a plot of the break stress of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 1000 mm/min.;

Figure 7 is a plot of the Water Vapor Permeability Coefficients (WVPC) of various neat polymer and blended polymer films as a function of the concentration of

ECOFLEX within the films, and an estimated trend line based on the lowest measured WVPC for a neat ECOFLEX film of 7.79 x $10^{-3}$ g·cm/$m^2$/d/mm Hg;

Figure 8 is a plot of the Water Vapor Permeability Coefficients (WVPC) of various neat polymer and blended polymer films as a function of the concentration of ECOFLEX within the films, and an estimated trend line based on the highest measured WVPC for a neat ECOFLEX film of 42 x $10^{-3}$ g·cm/$m^2$/d/mm Hg; and

Figure 9 is a plot of the modulus of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

### I. INTRODUCTION

The invention relates to fibrous sheets that are coated or impregnated with inventive biodegradable polymers or polymer blends. The treated fibrous sheets according to the invention are in many ways superior to conventional plastics that suffer from their inability to degrade when discarded into the environment, that are not readily printable absent special treatment, and that generally have poor dead-fold properties. The treated sheets can be engineered to have improved strength, flexibility, elongation, temperature stability, microwaveability, processability, and dead-fold.

In one aspect of the invention, a biodegradable polymer blend used to treat fibrous sheets includes at least one biopolymer having relatively high stiffness and at least one biopolymer having relatively high flexibility. When blended together, it is possible to derive the beneficial properties from each polymer while offsetting or eliminating the negative properties of each polymer when used separately.

In another aspect of the invention, one or more biodegradable polymers used to coat a fibrous sheet are blended with a significant quantity of an inorganic filler in order to greatly increase the heat stability of the resulting treated sheet. Fibrous sheets themselves tend to have greater heat stability compared to sheets and films formed using biodegradable polymers. Adding an inorganic filler to the biodegradable polymer or polymer blend (*e.g.*, in a concentration of at least about 30% by weight of the biodegradable polymer composition used to coat or impregnate the fibrous sheet) further increases the heat stability of treated sheets according to the invention. In the case of wraps used to protect food, such wraps can better withstand hot foods and being microwaved.

The treated sheets according to the invention are suitable for use as packaging materials, such as wraps, bags, pouches, coverings, laminate coatings, cartons, jugs, cups, plates, bowls, trays, platters, lids, straws, and the like.

Biodegradable polymers that may be used to treat fibrous sheets according to the present invention include, but are not limited to, synthetic polyesters, naturally derived polyesters, polyester amides, polycarbonates, and polyester urethanes, but may also include a variety of natural polymers and their derivatives, such as polymers and derivatives of starch, cellulose, other polysaccharides, and proteins. Particulate fillers, both organic and inorganic, may be incorporated into the polymers used to treat fibrous sheets to improve the dead-fold properties, increase bulk hand feel, create cavitation, reduce cost, and/or decrease self-adhesion of the treated sheets. Plasticizers may be added to impart desired softening and elongation properties. Treated fibrous sheets may optionally be embossed, crimped, quilted or otherwise textured to improve bulk hand feel and dead-fold. The biopolymers and biopolymer blends according to the invention more readily accept and retain print compared to conventional plastics or waxed papers because they typically include oxygen-containing moieties, such as ester, amide, or urethane groups, to which inks can readily adhere.

The terms "sheets" and "films" are to be understood as having their customary meanings as used in the thermoplastic and packaging arts Nevertheless, because the distinction between what constitutes a "sheet" and what constitutes a "film" largely turns on the thickness of the article of manufacture, the distinction is somewhat arbitrary (*i.e.* some articles may constitute both sheets and films). Because the biodegradable compositions according to the invention can be used to manufacture a wide variety of articles of manufacture, including articles useful to wrap, package or otherwise package food or other solid substrates, including sheets and films having a wide variety of thicknesses (both measured and calculated), it is not the intention of this disclosure to precisely distinguish, in all cases, between what may arguably constitute a "sheet" versus articles that may arguably constitute a "film". Therefore, when the present disclosure refers to "sheets and films" and "sheets or films", the intention is to designate the entire universe of articles of manufacture that may arguably constitute "sheets", "films" or both.

The terms "polymer blend" and "biodegradable polymer composition" includes two or more unfilled polymers and/or one or more polymers into which one or more types of solid fillers have been added.

The term "microwaveable" refers to biodegradable polymer compositions and treated sheets that can be placed together with food into a microwave oven and microwaved so as to heat the food without the composition melting or otherwise transferring from the treated sheet onto the food.

## II. TREATED SHEETS

Treated sheets according to the invention include any fibrous sheet that has been coated or impregnated with a biodegradable polymer blend to render the fibrous sheet more resistant to liquids, such as water, oils or solvents. Specific examples of fibrous sheets and biodegradable polymer blends that may be used to manufacture treated sheets within the scope of the invention will now be discussed in greater detail.

### A. Fibrous Sheets

It is within the scope of the invention to coat or impregnate various fibrous sheets known in the art. Examples include a wide variety of tissue papers, ordinary paper, paperboard, felts, wovens and nonwovens. In one embodiment, the fibrous sheet comprises a 12-15 lb/3000 $ft^2$ tissue paper. Coating or impregnating 12-15 lb/3000 $ft^2$ tissue paper yields treated sheets that are especially suitable for use as food wraps. It will be appreciated that it is within the scope of the invention to treat tissue papers and papers having a wide range of possible weights, *e.g.*, from 8 lb/3000 $ft^2$ to 60 lb/3000 $ft^2$.

### B. Biodegradable Polymers.

Biodegradable polymers that may be used within the scope of the present invention to coat or impregnate fibrous sheets include those which degrade through the action of living organisms, light, air, water and combinations of the foregoing. Such polymers include a range of synthetic polymers, such as polyesters, polyester amides, polycarbonates and the like. Naturally-derived semi-synthetic polyesters (*e.g.* from fermentation) can also be used. Biodegradation reactions are typically enzyme-catalyzed and generally occur in the presence of moisture. Natural macromolecules containing hydrolyzable linkages, such as protein, cellulose and starch, are generally susceptible to biodegradation by the hydrolytic enzymes of microorganisms. A few man-made polymers, however, are also biodegradable. The hydrophilic/hydrophobic character of polymers greatly affects their biodegradability, with more polar polymers being more readily biodegradable as a general rule. Other characteristics that affect polymer biodegradability include crystallinity, chain flexibility and chain length.

Besides being able to biodegrade, it is often important for a polymer or polymer blend to exhibit certain physical properties, such as stiffness, flexibility, water-resistance,

oil-resistance, solvent resistance, strength, elongation, temperature stability, moisture vapor transmission, gas permeability, and/or dead-fold. The intended application of a particular treated fibrous sheet will often dictate which properties are necessary in order for a particular polymer, polymer blend, or treated sheet manufactured therefrom to exhibit the desired performance criteria. When used to form treated sheets suitable for use as packaging materials, desired performance criteria may include elongation, dead-fold, strength, printability, imperviousness to liquids, breathability, temperature stability, and the like.

Because of the limited number of biodegradable polymers, it is often difficult, or even impossible, to identify one single polymer or copolymer which meets all, or even most, of the desired performance criteria for a given application. This is particularly true in the area of packaging materials. Polymers that have a high glass transition temperature ($T_g$) are often difficult, if not impossible, to blow or cast into films on a mass scale. On the other hand, polymers that have a very low glass transition temperature typically have relatively low softening and/or melting points, which makes them difficult to mass produce into sheets and films without the tendency of blocking, or self adhesion. Moreover, such sheets and films may lack adequate strength, water vapor barrier properties, high temperature stability, and/or modulus to be suitable for certain applications, such as in the manufacture of wraps or laminates coatings.

In one aspect of the invention, it has been discovered that compositions suitable for coating or impregnating fibrous sheets can be obtained by blending one or more "stiff", or high glass transition temperature, polymers with one or more "soft", or low glass transition temperature, polymers. In another aspect of the invention, polymers or polymer blends can be filled with particulate fillers, and/or treated sheets or films made therefrom can be textured, in order to yield sheets having improved dead-fold properties.

Notwithstanding the benefits that can be derived from using a blend of stiff and soft polymers, particularly when extruding or blowing films or sheets used to coat fibrous sheets, it will be appreciated that there are coating methods that do not require the formation of an extruded or blown film or sheet, such as spreading using a doctor blade or spray coating. In such cases, it may not be necessary to use a polymer blend. It may be desirable, however, to use water, a solvent, or plasticizer to increase the MFI to facilitate the coating or impregnation process. It may be desirable to incorporate a significant quantity of an inorganic filler (*e.g.* silica or limestone) in order to increase the heat

stability of the resulting treated sheet. In the case of a food wrap, increasing the heat stability increases the microwaveability of the treated sheet.

1. **Stiff Polymers.**

Even though the use of terms such as "stiff" and "soft" polymers may be somewhat arbitrary, such classifications are useful when determining which polymers to blend together in order to obtain a polymer blend having the desired performance criteria. In general, those polymers that may be characterized as being relatively "stiff", or less flexible, typically include polymers which have a glass transition temperature of at least about 10°C. Stiff polymers will preferably have a glass transition temperature of at least about 15°C., more preferably at least about 25°C., and most preferably at least about 35°C. The foregoing temperatures attempt to take into consideration the fact that the "glass transition temperature" is not always a discreet temperature but is often a range of temperatures within which the polymer changes from being a glassy and more brittle material to being a softer and more flexible material.

The glass transition temperature should be distinguished from the melting point of a polymer at or beyond which a thermoplastic polymer becomes plastic and deformable without significant rupture. Although there is often a positive correlation between a polymer's glass transition temperature ($T_g$) and its melting point ($T_m$), this is not strictly the case with all polymers. In some cases the difference between $T_g$ and $T_m$ may be large. In other cases it may be relatively small. It is generally the case, however, that the melting point of a stiffer polymer will typically be greater than the melting point of a softer polymer.

Preferred "stiff" polymers include, but are not limited to, modified polyethylene terephthalates (such as those manufactured by Du Pont), polyesteramides (such as those manufactured by Bayer), polylactic acid-based polymers (such as those manufactured by Cargill-Dow Polymers and Dianippon Ink), terpolymers based on polylactic acid, polyglycolic acid and polycaprolactone (such as those manufactured by Mitsui Chemicals), polyalkylene carbonates (such as polyethylene carbonate manufactured by PAC Polymers), and polyhydroxybutyrate (PHB).

A presently preferred stiff biopolymer includes a range of modified polyethylene terephthalate (PET) polymers manufactured by DuPont, and sold under the trade name BIOMAX. Various modified PET polymers of DuPont are described in greater detail in U.S. Patent No. 5,053,482 to Tietz, U.S. Patent No. 5,097,004 to Gallagher et al., U.S. Patent No. 5,097,005 to Tietz, U.S. Patent No. 5,171,308 to Gallagher et al., U.S. Patent

No. 5,219,646, to Gallagher et al., and U.S. Patent No. 5,295,985 to Romesser et al. For purposes of disclosing "stiff" polymers, the foregoing patents are disclosed herein by reference.

In general, the modified PET polymers of DuPont may be characterized as comprising alternating units of a terephthalate constituent and an aliphatic constituent, with the aliphatic constituent comprising a statistical distribution of two or more different aliphatic units derived from two or more different diols, such as ethylene glycol, diethylene glycol, triethylene oxide, polyethylene glycol, lower alkane diols, both branched and unbranched, and derivatives of the foregoing. A portion of the aliphatic units may also be derived from an aliphatic diacid, such as adipic acid. In addition, a fraction of the phenylene groups within the repeating terephthalate units may be sulfonated and neutralized with an alkali metal or alkaline earth metal base. Both the aliphatic portion of the modified PET polymer as well as the statistically significant quantity of sulfonated terephthalate units contribute significantly to the biodegradability of the BIOMAX polymer.

Some BIOMAX grades of polymers have a melting point of 200-208°C and a glass transition temperature of 40-60°C. BIOMAX 6926 is one such grade. It is a relatively strong and stiff polymer that, when blended with a softer polymer, yields a mixture that can readily be formed into sheets and films. In addition, or in the alternative, one or more particulate fillers may be included in order to impart desired properties described more fully herein.

In general, modified polyethylene terephthalates that would be expected to have properties suitable for use as a "stiff" biodegradable polymer consist essentially of recurring structural units having the following general formula:

$$—[—C(O)—R—C(O)—OGO—]_a—[—C(O)—Q—O—]_b—$$

wherein up to about 40 mole % of R is selected from the group consisting of a chemical bond and one or more divalent, non-aromatic, $C_1$-$C_{10}$ hydrocarbylene radicals, and the remainder of R is at least about 85% mole % p-phenylene radical,

wherein G includes from 0 to about 30 mole % of a polyethylene ether radical selected from the group consisting of:

$—(CH_2)_2—O—(CH_2)_2—$ and $—(CH_2)_2—O—(CH_2)_2—O—(CH_2)_2—$

and the remainder of G is selected from the group consisting of polyalkylene ether radicals of molecular weight at least about 250 (number average), and $—(CH_2)_2—$,

—$(CH_2)_3$—, and —$(CH_2)_4$— radicals,

wherein Q is derived from a hydroxy acid of the formula:

$$HO[—C(O)—Q—O—]_xH$$

wherein $x$ is an integer and such hydroxy acids have a melting point at least 5°C. below their decomposition temperature, and Q is selected from the group consisting of a chemical bond and hydrocarbylene radicals —$(CH_2)_n$—, where $n$ is an integer from 1 to 5, —C(R')H—, and —C(R')$HCH_2$—. wherein R' is selected from the group consisting of —$CH_3$ and —$CH_2CH_3$, and wherein "*a*" and "*b*" are mole fractions of the polymer, and the mole fraction "*a*" may be 0.6 to 1 and, correspondingly, mole fraction "*b*" may be 0 to 0.4, and wherein about 0.1 to about 15 mole %, preferably about 0.1 to about 2.5 mole %, of the polymer contains alkali metal or alkaline earth metal sulfo groups, especially about 1.5 to about 2 mole % of such groups.

Another stiff biopolymer that may be used in manufacturing polymer blends according to the present invention includes polylactic acid (PLA). Polylactic acid typically has a glass transition temperature of about 59°C. and a melting point of about 178°C. PLA has low elongation and is quite hard. It is a strong thermoplastic material that can be injection molded, extruded, cast, thermoformed, or used as spun or melt-blown fibers to produce nonwoven goods.

Polymers based on or including PLA first found commercial application as medical sutures in 1970. High polymers of lactic acid ($M_n$=50,000-110,000) are strong thermoplastics that can be fabricated into useful products that can be broken down by common soil bacteria. Potential applications of PLA include paper coatings for packaging (food and beverage cartons), plastic foam for fast foods, microwavable containers, and other consumer products such as disposable diapers or yard waste bags. PLA can be a homopolymer or it may be copolymerized with glycolides, lactones or other monomers. One particularly attractive feature of PLA-based polymers is that they are derived from renewable agricultural products.

Because lactic acid is difficult to polymerize directly to high polymers in a single step on a commercial scale, most companies employ a two-step process. Lactic acid is first oligomerized to a linear chain with a molecular weight of less than 3000 by removing water. The oligomer is then depolymerized to lactide, which is a cyclic dimer consisting of two condensed lactic acid molecules. This six-member ring is purified and

subjected to ring opening polymerization to produce polylactic acid with a molecular weight of 50,000-110,000.

Because lactic acid has an asymmetric carbon atom, it exists in several isomeric forms. The lactic acid most commonly sold commercially contains equal parts of L-(+)-lactic acid and D-(-)-lactic acid and is therefore optically inactive, with no rotatory power. The racemic mixture is called DL-lactic acid.

Another stiff polymer that may be used within the inventive polymer blends is known as CPLA, which is a derivative of PLA and is sold by Dianippon Ink. Two classes of CPLA are sold and are referred to as "CPLA hard" and "CPLA soft", both of which comprise "stiff polymers", as that term has been defined herein. CPLA hard has a glass transition temperature of 60°C., while CPLA soft has a glass transition temperature of 51°C.

Bayer corporation manufactures polyesteramides sold under the name BAK. Polyester amides manufactured by Bayer are described more fully in U.S. Patent No. 5,644,020 to Timmermann et al. For purposes of disclosing biodegradable polymers, at least some of which constitute "stiff" polymers, the foregoing patent is incorporated herein by reference. One form of BAK is prepared from adipic acid, 1,4-butanediol, and 6-aminocaproic acid. BAK 1095, a polyesteramide having an $M_n$ of 22,700 and an $M_w$ of 69,700 and which contains aromatic constituents, has a melting point of 125°C. BAK 2195 has a melting point of 175°C. Although the glass transition temperatures of BAK 1095 and BAK 2195 are difficult to measure, because BAK appears to behave like a stiff polymer in the sense that improved properties may be obtained by blending BAK with a soft polymer, the inventors believe that the glass transition temperature of BAK polymers is essentially at least about 10°C. For purposes of understanding the meaning and scope of the specification and claims, polyester amides such as BAK, as well as others that behave like BAK and can be used as a "stiff" polymer, shall be deemed to have a glass temperature of at least about 10°C.

Mitsui Chemicals, Inc. manufactures a terpolymer that includes units derived from polylactide, polyglycolide and polycaprolactone that have been condensed together. Thus, this polymer is an aliphatic polymer and may be characterized as a PLA/PGA/PCL terpolymer. Three grade of this polymer are available, H100J, S100 and T100. The H100J grade PLA/PGA/PCL terpolymer has been analyzed to have a glass transition temperatures of 74°C. and a melting point of 173°C.

PAC Polymers Inc. manufactures polyethylene carbonate (PEC) having a glass transition temperature range of 10-28°C. PEC is a "stiff" polymer for purposes of the present invention.

Polyhydroxybutyrates (PHBs) can act as either a stiff or soft polymer depending on their molecular weight, whether they have been modified using chain extenders and/or branching agents, whether they have been copolymerized with another polymer, and depending on the other constituents within the overall thermoplastic composition. In this sense, PHBs are unique among biopolymers and may be of special interest for use in making wraps, laminate coatings, packaging materials, and the like.

As discussed more fully below, native or dried gelatinized starch can be used as particulate fillers in order to increase the dead-fold properties of sheets and films made from a particular polymer or polymer blend. However, to the extent that starches become thermoplastic but retain a substantially portion of their crystallinity, such starches may act as "stiff", rather than "soft", polymers.

**2. Soft Polymers.**

In general, those biopolymers that may be characterized as being "soft", or less rigid, typically include polymers which have a glass transition temperature of less than about 0°C. Soft biopolymers within the scope of the invention will typically have a glass transition temperature of less than about 0°C., preferably less than about –4°C., more preferably less than about –10°C., more especially preferably less than about –20°C., and most preferably less than about –30°C. The foregoing temperatures attempt to take into consideration the fact that the "glass transition temperatures" of "soft" polymers are not always discreet temperatures but often comprise a range of temperatures.

Preferred "soft" biopolymers within the scope of the present invention include, but are not limited to, aliphatic-aromatic copolyesters (such as those manufactured by BASF and Eastman Chemical), aliphatic polyesters which include repeating units having at least 5 carbon atoms, *e.g.*, polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate copolymer and polycaprolactone (such as those manufactured by Daicel Chemical, Monsanto, Solvay, and Union Carbide), and succinate-based aliphatic polymers, *e.g.*, polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and polyethylene succinate (PES) (such as those manufactured by Showa High Polymer).

U.S. Patent Nos. 5,817,721, 5,863,991, 5,880,220, 5,889,135, 5,936,045, 6,018,004, 6,046,248, 6,111,058, 6,114,042, 6,201,034, 6,258,924, 6,297,347, 6,303,677, 6,353,084, all to Warzelhan et al., and assigned to BASF, disclose a range of aliphatic-

aromatic copolyesters within the scope of the invention, as do U.S. Patent No. 6,103,058 to Yamamoto et al. and U.S. Patent No. 6,120,895 to Kowitz et al. Similarly, U.S. Patent Nos. 5,292,783, 5,446,079, 5,559,171, 5,580,911, 5,599,858 and 5,900,322, all to Buchanan et al. and assigned to Eastman Chemical, as well as U.S. Patent Nos. 6,020,393 and 6,922,829 to Khemani, also assigned to Eastman Chemical, disclose aliphatic-aromatic copolyesters within the scope of the invention. For purposes of disclosing "soft" polymers, the foregoing patents are incorporated herein by reference.

A preferred "soft" polymer that may be used in the manufacture of polymer blends includes aliphatic-aromatic copolyesters manufactured by BASF and sold under the trade name ECOFLEX. The aliphatic-aromatic copolyesters manufactured by BASF comprise a statistical copolyester derived from 1,4-butanediol, adipic acid, and dimethylterephthalate (DMT). In some cases, a diisocyanate is used as a chain lengthener. Branching agents may also be used to yield branched, rather than linear, copolymers.

Copolymerization of aliphatic monomers, such as diols and diacids, with aromatic monomers, such as diols and diacids (*e.g.*, terephthalic acid or diester derivatives such as DMT), is one way to improve the performance properties of aliphatic polyesters. However, questions have been raised within the industry regarding the complete biodegradability of aliphatic-aromatic copolyesters because aromatic copolyesters such as PET are known to be resistant to microbial attack. Nevertheless, researchers have discovered that aliphatic-aromatic copolyesters are indeed biodegradable and that the biodegradability of these copolyesters is related to the length of the aromatic sequence. Block copolyesters with relatively long aromatic sequences are less rapidly degraded by microorganisms compared to random copolyesters having more interrupted aromatic sequences. Film thickness is also a factor, with thicker films degrading more slowly due to their reduced surface to volume ratio than thinner films, all things being equal. The polymer presently sold under the name ECOFLEX S BX 7000 by BASF has a glass transition temperature of −33°C. and a melting range of 105-115°C.

Another "soft" aliphatic-aromatic copolyester is manufactured by Eastman Chemical Company and is sold under the trade name EASTAR BIO. The aliphatic-aromatic copolyester manufactured by Eastman is a random copolymer derived from 1,4-butanediol, adipic acid, and dimethylterephthalate (DMT). One particular grade of EASTAR BIO, known as EASTAR BIO 14766, has a glass transition temperature of −33°C and a melting point of 112°C. It has a tensile strength at break in the machine

direction of 19 MPa, an elongation at break of 600%, and a tensile modulus of elasticity of 97 MPa (tangent). It has an Elmendorf tear strength of 282 g.

Polycaprolactone (PCL) is a biodegradable aliphatic polyester having a relatively low melting point and a very low glass transition temperature. It is so named because it is formed by polymerizing ε-caprolactone. The glass transition temperature of PCL is −60°C. and the melting point is only 60°C. Because of this PCL and other similar aliphatic polyesters with low melting points are difficult to process by conventional techniques such as film blowing and blow molding. Films made from PCL are tacky as extruded and have low melt strength over 130°C. Also, the slow crystallization of this polymer causes the properties to change over time. Blending PCL with other polymers improves the processability of PCL. One common PCL is TONE, manufactured by Union Carbide. Other manufactures of PCL include Daicel Chemical, Ltd. and Solvay. Though the use of PCL is certainly within the scope of the invention, it is currently a less preferred soft biopolymer than aliphatic-aromatic polyesters, which give overall better performance.

ε-Caprolactone is a seven member ring compound that is characterized by its reactivity. Cleavage usually takes place at the carbonyl group. ε-Caprolactone is typically made from cyclohexanone by a peroxidation process. PCL is a polyester made by polymerizing ε-caprolactone. Higher molecular weight PCL may be prepared under the influence of a wide variety of catalysts, such as aluminum alkyls, organometallic compositions, such as Group Ia, IIa, IIb, or IIIa metal alkyls, Grignard reagents, Group II metal dialkyls, calcium or other metal amides or alkyl amides, reaction products of alkaline earth hexamoniates, alkaline oxides and acetonitrile, aluminum trialkoxides, alkaline earth aluminum or boron hydrides, alkaline metal or alkaline earth hydrides or alkaline metals alone. PCL is typically prepared by initiation with an aliphatic diol (HO-R-OH), which forms a terminal end group.

Another "soft" aliphatic polyester that may be used in manufacturing the inventive polymer blends is polyhydroxybutyrate-hydroxyvalerate copolymer (PHBV), which is manufactured using a microbial-induced fermentation process. One such PHBV copolyester, manufactured by the Monsanto Company, has a glass transition temperature of about 0°C. and a melting point of about 170°C. If possible, PHBV copolyesters should be formulated and/or modified so as have a glass transition temperature less than about −5°C.

In the fermentation process used to manufacture PHBV, a single bacterium species converts corn and potato feed stocks into a copolymer of polyhydroxybutyrate and hydroxyvalerate constituents. By manipulating the feed stocks, the proportions of the two polymer segments can be varied to make different grades of material. All grades are moisture resistant while still being fully biodegradable. The world producers of PHBV are Monsanto, with its BIOPOL product, and METABOLIX, with its various grades of polyhydroxy-alkanoates (PHAs). Polyhydroxyvalerate (PHV) is also an example of a "soft" polymer.

As set forth above, polyhydroxybutyrates (PHBs) can act as either a stiff or soft polymer depending on their molecular weight, whether they have been modified using chain extenders and/or branching agents, whether they have been copolymerized with another polymer, and depending on the other constituents within the overall thermoplastic composition. In this sense, PHBs are unique among biopolymers and may be of special interest for use in making wraps, laminate coatings, packaging materials, and the like.

Another class of "soft" aliphatic polyesters are based on repeating succinate units such as polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and polyethylene succinate (PES). Each of these succinate-based aliphatic polyesters are manufactured by Showa High Polymer, Ltd. and are sold under the trade name BIONELLE. PBS (Bionolle 1001) has a glass transition temperature of −30°C. and a melting point of 114°C. PBSA (Bionolle 3001) has a glass transition temperature of −35°C. and a melting point of 95°C. PES (Bionolle 6000) has a glass transition temperature of −4°C. and a melting point of 102° .

The target applications for BIONOLLE include films, sheets, filaments, foam-molded products and foam-expanded products. BIONOLLE is biodegradable in compost, in moist soil, in water with activated sludge, and in sea water. PBSA degrades rapidly in a compost environment, so it is similar to cellulose, whereas PBS degrades less rapidly and is similar to newspaper in terms of biodegradation.

BIONOLLE is manufactured according to a patented two-step process of preparing succinate aliphatic polyesters with high molecular weights and useful physical properties. In a first step, a low molecular weight hydroxy-terminated aliphatic polyester prepolymer is made from a glycol and an aliphatic dicarboxylic acid. This polymerization is catalyzed by a titanium catalyst such as tetraisopropyltitanate, tetraisopropoxy titanium, dibutoxydiacetoacetoxy titanium, or tetrabutyltitanate. In the

second step, a high molecular weight polyester is made by reacting a diisocyanate, such as hexamethylene diisocyante (HMDI) with a polyester prepolymer.

Showa manufactures PBS by first reacting 1,4-butanediol with succinic acid in a condensation reaction to form a prepolymer and then reacting the prepolymer with HMDI as a chain extender.

PBSA copolymer is manufactured by first condensing 1,4-butanediol, succinic acid and adipic acid to form a prepolymer and then reacting the prepolymer with HMDI as a chain extender.

PES homopolymer is prepared by reacting ethylene glycol and succinic acid and using HMDI or diphenylmethane diisocyanate as a chain extender.

Succinate-based aliphatic polyesters are also manufactured by Mitsui Toatsu, Nippon Shokubai, Cheil Synthetics, Eastman Chemical, and Sunkyon Industries.

Finally, although starch, such as modified starch or starch that has been gelatinized with water and subsequently dried, is known to have a high glass transition temperature (*i.e.*, 70-85°C.) and be very crystalline at room temperature, certain forms of starch in which the crystallinity has been greatly reduced or destroyed altogether can have very low glass transition temperatures and may, in fact, constitute "soft" biodegradable polymers within the scope of the invention. As discussed more fully below, native or dried gelatinized starch can be used as particulate fillers in order to increase the dead-fold properties of sheets and films made from a particular polymer or polymer blend. Moreover, to the extent that starches become thermoplastic but retain a substantially portion of their crystallinity, such starches may act as "stiff", rather than "soft", polymers. Nevertheless, there exists a range of thermoplastic starch polymers that can behave as "soft" polymers.

For example, U.S. Patent No. 5,362,777 to Tomka is a landmark patent and was the first attempt to manufacture what is known as thermoplastically processable starch (TPS). TPS is characterized as a thermoplastic starch polymer formed by mixing and heating native or modified starch in the presence of an appropriate high boiling plasticizer (such as glycerin and sorbitol) in a manner such that the starch has little or no crystallinity, a low glass transition temperature, and very low water (less than 5%, preferably less than about 1% by weight while in a melted state after venting and prior to conditioning). When blended with appropriate hydrophobic polymers, such as the stiff polymers disclosed herein, *e.g.*, polyesteramides such as BAK, TPS can have a glass transition temperature as low as −60°C, and typically below about −20°C.

Although it is within the scope of the invention to include thermoplastic polymers based on starch that include plasticizers such as glycerine, sorbitol, propylene glycol and the like, it is preferable, when manufacturing packaging materials that will come into contact with food products, to utilize thermoplastic starch polymers that are made without the use of such plasticizers, which can potentially diffuse into food. Preferred thermoplastic starch polymers for use in making food wraps may advantageously utilize the natural water content of native starch granules to initially break down the granular structure and melt the native starch. Thereafter, the melted starch can be blended with one or more synthetic biopolymers, and the mixture dried by venting, in order to yield a final polymer blend. Where it is desired to make food wraps or other sheets or films intended to contact food using a thermoplastic starch polymer made with a high boiling liquid plasticizer, it will be preferable to limit the quantity of such thermoplastic starch polymers to less than 10% by weight of the polymer mixture, exclusive of any solid fillers.

**C. OTHER COMPONENTS.**

There are a number of optional components which may be included within the biodegradable polymer blends in order to impart desired properties. These include, but are not limited to, plasticizers, lubricants, fillers, natural polymers and nonbiodegradable polymers.

**1. Plasticizers and Lubricants.**

Plasticizers and lubricants may optionally be added in order to improve processing, such as extrusion, film blowing, spreading or spraying, or final mechanical properties, particularly of polymer blends that are relatively stiff. A stiffer polymer blend may be dictated by other performance criteria, such as high temperature stability, strength, lower elongation, higher dead-fold, resistance to "blocking" during and after processing, and the like. In such cases, a plasticizer may allow the polymer blend to satisfy certain processing and/or performance criteria.

In the case where a biodegradable polymer or polymer blend is spread or sprayed onto a fibrous sheet, it may be advantageous to use a plasticizer to increase the melt flow index (MFI) of the molten polymer or polymer blend. Increasing the MFI of a molten polymer or polymer blend facilitates high speed coating. In general, when certain biodegradable polymers are heated to above their softening point, they have an MFI between about 2-10 g/10 min. Increasing the MFI preferably to at least about 40 g/10 min., more preferably to at least about 70 g/10 min., and most preferably to at least about

100 g/10 min. greatly facilitates spreading or spraying a molten biodegradable polymer blend.

Suitable plasticizers within the scope of the invention, particularly when incorporated into a polymer blend that is intended to be used in the manufacture of wraps and other packaging materials that will come into contact with food, will preferably be safe if consumed, at least in smaller quantities.

Exemplary plasticizers that may be used in accordance with the present invention include, but are not limited to, soybean oil, caster oil, TWEEN 20, TWEEN 40, TWEEN 60, TWEEN 80, TWEEN 85, sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan trioleate, sorbitan monostearate, PEG, derivatives of PEG, N,N-ethylene bis-stearamide, N,N-ethylene bis-oleamide, polymeric plasticizers such as poly(1,6-hexamethylene adipate), and other compatible low molecular weight polymers.

Examples of lubricants include salts of fatty acids, an example of which is magnesium stearate.

Volatile plasticizers that can be removed during or after the coating process, such as water or volatile solvents, may be used to facilitate high speed coating. Examples of volatile solvents that may be used, preferably by recovering and reusing such solvents, include, but are not limited to, chloroform, methylene chloride, other chlorinated hydrocarbons, ethyl alcohol, isopropyl alcohol, other alcohols, acetone, methyl ethyl ketone, other ketones, and the like.

It has been found, for example, that including 200 ppm water increases the MFI of a molten biodegradable polymer composition from 4 g/10 min. to about 40 g/10 min. Whereas many of the biodegradable polymers described herein are "hydrophobic" in the sense that they do not dissolve or degrade when exposed to water at room temperature, they do contain polar moieties that greatly increase the affinity of such polymers for water while heated to a molten state. Thus, it is possible to blend some amount of water within molten a biodegradable polymer that would otherwise be hydrophobic when cooled to room temperature.

**2. Solid Fillers.**

Particulate fillers may optionally be added for a number of reasons, including but not limited to, increasing the Young's modulus, dead-fold properties, rigidity, breathability, thermal stability, microwaveability, and insulating ability, and for decreasing the cost and tendency of the polymer blend to "block" or self-adhere during processing. Other fillers, like fibers having a high aspect ratio, may increase the strength,

fracture energy and dead-fold properties of the sheets and films according to the invention. In general, fillers within the scope of the invention will generally fall within three classes or categories: (1) inorganic particulate fillers, (2) fibers and (3) organic fillers.

**a. Inorganic Particulate Fillers**

The terms "particle" or "particulate filler" should be broadly interpreted to include filler particles having any of a variety of different shapes and aspect ratios. In general, "particles" are those solids having an aspect ratio (*i.e.*, the ratio of length to thickness) of less than about 10:1. Solids having an aspect ratio greater than about 10:1 may be better understood as "fibers", as that term will be defined and discussed hereinbelow.

Virtually any known filler, whether inert or reactive, can be incorporated into the biodegradable polymer blends. In general, adding an inorganic filler will tend to reduce the cost of the resulting polymer blend. If a relatively small amount of inorganic filler is used, the effects on the properties of the final composition are minimized, while adding a relatively large amount of inorganic filler will increase those effects. In those cases where adding the inorganic filler will tend to detract from a critical physical parameter, such as tensile strength or flexibility, only so much of the filler should be added in order to reduce the cost of the resulting composition, while retaining adequate mechanical properties required by the intended use. However, in those cases where adding the inorganic filler will improve one or more desired physical properties of a given application, such as stiffness, compressive strength, dead-fold, heat resistance, microwaveability, insulating ability, and/or breathability, it may be desirable to increase the quantity of added filler in order to provide this desired property while also proving greatly decreased cost.

It will be appreciated that one of ordinary skill in the art, using a microstructural engineering approach, can select the types and amount of the various inorganic fillers that may be included within the polymer blend in order to engineer a final material having the desired properties while taking advantage of the cost-reducing properties of adding the inorganic filler.

In general, in order to maximize the quantity of inorganic filler while minimizing the deleterious mechanical effects of adding the filler as much as possible, it may be advantageous to select filler particles in a manner that decreases the specific surface area of the particles. The specific surface area is defined as the ratio of the total particle surface area versus the total particle volume. One way to decrease the specific surface

area is to select particles that have a more uniform surface geometry. The more jagged and irregular the particle surface geometry, the greater will be the ratio of surface area to volume of that particle. Another way to decrease the specific surface area is to increase the particle size. In view of the advantages of decreasing the specific surface area of the inorganic filler, it will be preferable to include inorganic filler particles having a specific surface area in a range from about 0.1 $m^2/g$ to about 400 $m^2/g$, more preferably in range from about 0.15 $m^2/g$ to about 50 $m^2/g$, and most preferably in a range from about 0.2 $m^2/g$ to about 2 $m^2/g$.

Related to decreased specific surface area in improving the rheology and final strength properties of the polymer blends of the present invention is the concept of particle packing. Particle packing techniques allow for a reduction in "wasted" interstitial space between particles while maintaining adequate particle lubrication and, hence, mixture rheology, within the melted polymer blend, while also allowing for more efficient use of the thermoplastic phase as a binder in the final hardened polymer blends of the present invention. Simply stated, particle packing is the process of selecting one or more ranges of particle sizes in order that the spaces between larger particles are substantially occupied by a selected group of smaller particles.

In order to optimize the packing density of the inorganic filler particles, differently sized particles having sizes ranging from as small as about 0.01 micron to as large as about 2 mm may be used. Of course, the thickness and other physical parameters of the desired article to be manufactured from any given polymer blend may often dictate the upper particle size limit. In general, the particle packing will be increased whenever any given set of particles is mixed with another set of particles having an average particle size (*i.e.*, width and/or length) that is at least about 2 times bigger or smaller than the average particle size of the first group of particles. The particle packing density for a two-particle system will be maximized whenever the size ratio of a given set of particles is from about 3-10 times the size of another set of particles. Similarly, three or more different sets of particles may be used to further increase the particle packing density.

The degree of packing density that will be "optimal" will depend on a number of factors including, but not limited to, the types and concentrations of the various components within both the thermoplastic phase and the solid filler phase, the shaping method that will be employed, and the desired mechanical and other performance properties of the final articles to be manufactured from a given polymer blend. One of ordinary skill in the art will be able to determine the optimal level of particle packing that

will optimize the packing density through routine testing. A more detailed discussion of particle packing techniques can be found in U.S. Patent No. 5,527,387 to Andersen et al. For purposes of disclosing particle packing techniques that may be useful in maximizing or optimizing particle packing density, the foregoing patent is incorporated herein by reference.

In those cases where it is desired to take advantage of the improved properties of rheology and binding efficiency utilizing particle packing techniques, it will be preferable to include inorganic filler particles having a natural particle packing density in a range from about 0.55 to about 0.95, more preferably in range from about 0.6 to about 0.9, and most preferably in a range from about 0.7 to about 0.85.

Examples of useful inorganic fillers that may be included within the biodegradable polymer blends include such disparate materials as sand, gravel, crushed rock, bauxite, granite, limestone, sandstone, glass beads, aerogels, xerogels, mica, clay, alumina, silica, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, gypsum dihydrate, insoluble salts, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium aluminate, magnesium carbonate, titanium dioxide, talc, ceramic materials, pozzolanic materials, salts, zirconium compounds, xonotlite (a crystalline calcium silicate gel), lightweight expanded clays, perlite, vermiculite, hydrated or unhydrated hydraulic cement particles, pumice, zeolites, exfoliated rock, ores, minerals, and other geologic materials. A wide variety of other inorganic fillers may be added to the polymer blends, including materials such as metals and metal alloys (*e.g.*, stainless steel, iron, and copper), balls or hollow spherical materials (such as glass, polymers, and metals), filings, pellets, flakes and powders (such as microsilica).

The particle size or range of particle sizes of the inorganic fillers will depend on the wall thickness of the film, sheet, or other article that is to be manufactured from the polymer blend. In general, the larger the wall thickness, the larger will be the acceptable particle size. In most cases, it will be preferable to maximize the particle size within the acceptable range of particle sizes for a given application in order to reduce the cost and specific surface area of the inorganic filler. For films that are intended to have a substantial amount of flexibility, tensile strength, bending endurance and relatively low dead-fold and breathability (*e.g.*, plastic bags) the particle size diameter of the inorganic filler will preferably be less than about 20% of the wall thickness of the film. For example, for a film or sheet having a thickness of 40 microns, it may be preferable for the inorganic filler particles to have a particle size diameter of about 8 microns or less.

On the other hand, it may be desirable in some cases for at least a portion of the filler particles to have a larger particle size diameter, such as a diameter that is equal to or greater than the thickness of the polymeric sheet or film. Utilizing filler particles whose diameters equal or exceed the thickness of the polymeric sheet or film disrupts the surface of the sheet or film and increases the surface area, which can advantageously increase the bulk-hand-feel and/or dead-fold properties of the sheet or film. In the case where the sheets or films are mono or biaxial stretched, the use of larger filler particles (*e.g.*, larger than 20% of the wall thickness of the film) creates definitive discontinuities that yield sheets and films having a high degree of cavitation. Cavitation results in sheets having a touch and feel that more closely resembles the touch and feel of paper. In addition, it greatly increases the breathability and water vapor transmission of the sheets and films.

The amount of particulate filler added to a polymer blend will depend on a variety of factors, including the quantity and identities of the other added components, as well as the specific surface area, packing density, and/or size distribution of the filler particles themselves. Accordingly, the concentration of particulate filler within the polymer blends may be included in a broad range from as low as 0% by volume to as high as about 90% by volume of the polymer blend. Because of the variations in density of the various inorganic fillers than can be used, it may be more correct in some instances to express the concentration of the inorganic filler in terms of weight percent rather than volume percent. In view of this, the inorganic filler components can be included within a broad range from as low as 0% by weight to as high as 95% by weight of the polymer blend, preferably in a range from about 5% to about 90% by weight.

In those cases where it is desired for the properties of the thermoplastic phase to predominate due to the required performance criteria of the articles being manufactured, the inorganic filler will preferably be included in an amount in a range from about 5% to about 50% by volume of polymer blend. On the other hand, where it is desired to create highly inorganically filled systems, the inorganic filler will preferably be included in an amount in a range from about 50% to about 90% by volume.

In light of these competing objectives, the actual preferred quantity of inorganic filler may vary widely. In general terms, however, in order to appreciably decrease the cost of the resulting polymer blend and/or to impart increased dead-fold, heat-resistance, insulation ability, and/or microwaveability, the inorganic filler component will typically be included in an amount of at least about 10% by weight of the overall composition, preferably at least about 15% by weight, more preferably at least about 20% by weight,

more especially preferably at least about 30% by weight, and most preferably at least about 35% by weight of the overall composition.

**b. Discrete Fibers**

In addition to the fibrous sheet being treated, discrete fibers can optionally be used in order to improve the physical properties of the polymer blends. Like the aforementioned fillers, fibers will typically constitute a solid phase that is separate and distinct from the thermoplastic phase. However, because of the shape of fibers, *i.e.*, by having an aspect ratio greater than at least about 10:1, they are better able to impart strength and toughness than particulate fillers. As used in the specification and the appended claims, the terms "fibers" and "fibrous material" include both inorganic fibers and organic fibers. Fibers may be added to the moldable mixture to increase the flexibility, ductility, bendability, cohesion, elongation ability, deflection ability, toughness, dead-fold, and fracture energy, as well as the flexural and tensile strengths of the resulting sheets and articles.

Fibers that may be incorporated into the polymer blends include naturally occurring organic fibers, such as cellulosic fibers extracted from wood, plant leaves, and plant stems. In addition, inorganic fibers made from glass, graphite, silica, ceramic, rock wool, or metal materials may also be used. Preferred fibers include cotton, wood fibers (both hardwood or softwood fibers, examples of which include southern hardwood and southern pine), flax, abaca, sisal, ramie, hemp, and bagasse because they readily decompose under normal conditions. Even recycled paper fibers can be used in many cases and are extremely inexpensive and plentiful.

The fibers used in making the sheets and other articles of the present invention preferably have a high length to width ratio (or "aspect ratio") because longer, narrower fibers can impart more strength to the polymer blend while adding significantly less bulk and mass to the matrix than thicker fibers. The fibers will have an aspect ratio of at least about 10:1, preferably greater than about 25:1, more preferably greater than about 50:1, and most preferably greater than about 100:1.

The amount of fibers added to the polymer blends will vary depending upon the desired properties of the finished article of manufacture, with tensile strength, toughness, flexibility, and cost being the principle criteria for determining the amount of fiber to be added in any mix design. Accordingly, the concentration of fibers within the polymer blends of the present invention can be included in a broad range from 0% to about 90% by weight of the polymer blend. If included at all, fibers will preferably be included in an

amount in a range from about 1% to about 80% by weight of the polymer blend, more preferably in a range from about 3% to about 50% by weight, and most preferably in a range from about 5% to about 30% by weight of the polymer blend.

**c. Organic Fillers**

The polymer blends may also include a wide range of organic fillers. Depending on the melting points of the polymer blend and organic filler being added, the organic filler may remain as a discrete particle and constitute a solid phase separate from the thermoplastic phase, or it may partially or wholly melt and become partially or wholly associated with the thermoplastic phase.

Organic fillers may comprise a wide variety of natural occurring organic fillers such as, for example, seagel, cork, seeds, gelatins, wood flour, saw dust, milled polymeric materials, agar-based materials, native starch granules, pregelatinized and dried starch, expandable particles, and the like. Organic fillers may also include one or more synthetic polymers of which there is virtually endless variety. Because of the diverse nature of organic fillers, there will not generally be a preferred concentration range for the optional organic filler component.

Organic fillers can partially or wholly take the place of inorganic fillers. In some cases, organic fillers can be selected that will impart the same properties as inorganic fillers, such as to increase dead-fold, the bulk hand feel, breathability and water vapor transmission. When included at all, the organic filler component will typically be included in an amount of at least about 5% by weight of the overall composition, preferably at least about 10% by weight, more preferably at least about 20% by weight, and more especially preferably at least about 30% by weight, and most preferably at least about 35% by weight of the overall composition.

**3. Natural Polymers.**

In addition to thermoplastic starch or starch particles, other natural polymers that may be used within the polymer blends comprise or are derivatives of cellulose, other polysaccharides, polysaccharide gums and proteins.

Examples of starches and starch derivatives include, but are not limited to, modified starches, cationic and anionic starches, and starch esters such as starch acetate, starch hydroxyethyl ether, alkyl starches, dextrins, amine starches, phosphates starches, and dialdehyde starches.

Examples of derivatives of cellulose include, but are not limited to, cellulosic esters (*e.g.*, cellulose formate, cellulose acetate, cellulose diacetate, cellulose propionate,

cellulose butyrate, cellulose valerate, mixed esters, and mixtures thereof) and cellulosic ethers (*e.g.*, methylhydroxyethylcellulose, hydroxymethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose, and mixtures thereof).

Other polysaccharide-based polymers that can be incorporated into the polymer blends of the invention include alginic acid, alginates, phycocolloids, agar, gum arabic, guar gum, acacia gum, carrageenan gum, furcellaran gum, ghatti gum, psyllium gum, quince gum, tamarind gum, locust bean gum, gum karaya, xanthan gum, and gum tragacanth, and mixtures or derivatives thereof.

Suitable protein-based polymers include, for example, Zein® (a prolamine derived from corn), collagen (extracted from animal connective tissue and bones) and derivatives thereof such as gelatin and glue, casein (the principle protein in cow milk), sunflower protein, egg protein, soybean protein, vegetable gelatins, gluten and mixtures or derivatives thereof.

**4. Non Biodegradable Polymers.**

Although polymer blends preferably include biodegradable polymers, it is certainly within the scope of the invention to include one or more polymers which are not biodegradable. If the nonbiodegradable polymer generally comprises a disperse phase rather than the dominant continuous phase, polymer blends that include a nonbiodegradable polymer will nevertheless be biodegradable, at least in part. When degraded, the polymer blend may leave behind a nonbiodegradable residue that nevertheless is superior to the waste left behind by sheets and films that are entirely made of nonbiodegradable polymers.

Examples of common nonbiodegradable polymers suitable for forming sheets and films include, but are not limited to, polyethylene, polypropylene, polybutylene, PET, PETG, PETE, polyvinyl chloride, PVDC, polystyrene, polyamides, nylon, polycarbonates, polysulfides, polysulfones, copolymers including one or more of the foregoing, and the like.

**D. Polymer Blends.**

**1. Concentration Ranges of Biodegradable Polymers.**

The concentrations of the various components within the polymer blends used to treat fibrous sheets will depend on a number of factors, including the desired physical and mechanical properties of the treated sheet, the performance criteria of articles to be

manufactured from a treated sheet, the processing equipment used to manufacture and convert the blends and treated sheets into the desired article of manufacture, and the particular components within the blends. One of ordinary skill in the art will be able, in light of the specific examples and other teachings disclosed herein, to select and optimize the concentrations of the various components through routine testing.

In view of the wide variety of polymer blends within the scope of the invention, as well as the wide variety of different properties that may be engineered within the blends, the hard and soft polymers may be included within widely varying concentration ranges. In those cases where the polymer blend or composition includes a blend of stiff and soft biodegradable polymers, the one or more stiff biodegradable polymers within the inventive blends may have a concentration in a range from about 20% to about 99% by weight of the biodegradable polymers exclusive of the fibrous sheet and any fillers, preferably a concentration of at least about 30% by weight of the polymer blend, more preferably at least about 40% by weight of the polymer blend, more especially preferably greater than, but not including, 50% by weight of the polymer blend, and most preferably at least about 55% by weight of the polymer blend.

Similarly, when a blend of stiff and soft polymers is employed, the soft polymers may have a concentration in a range from about 1% to about 80% by weight of the biodegradable polymers exclusive of the fibrous sheet and any fillers, preferably a concentration up to about 70% by weight of the polymer blend, more preferably up to about 60% by weight of the polymer blend, more especially preferably less than, but not including, 50% by weight of the polymer blend, and most preferably up to about 45% by weight of the polymer blend.

The foregoing concentrations are measured in terms of the blend of hard and soft polymers exclusive of any optional components that may be added, as described and identified above.

**2. <u>Properties of Polymer Blends and Treated Sheets</u>.**

The polymer blends may be engineered to have a variety of desired properties as described herein. The properties of the final treated fibrous sheet will depend on a number of factors, including mix design of the polymer blend, processing conditions, post-formation processing, product size, particularly thickness, and the like. In the case of treated sheets intended to be used as "wraps", such as wraps used to enclose meats, other perishable food items, and especially fast food items (*e.g.*, sandwiches, burgers and dessert items), it will generally be desirable to provide treated sheets having good "dead-

fold" properties so that once folded, wrapped or otherwise manipulated into a desired orientation, such wraps will tend to maintain their orientation so as to not spontaneously unfold or unwrap, as which occurs with a large number of plastic sheets and films (*e.g.*, polyethylene).

In order to improve the dead-fold properties of treated sheets biodegradable polymers may be selected which yield blends having a relatively high Young's modulus, preferably at least about 100 MPa, more preferably at least about 150 MPa, and most preferably at least about 200 MPa. In general, increasing the concentration of the stiff biodegradable polymer will tend to increase the Young's modulus. The Young's modulus may also be increased by loading the polymer blends with one or more fillers, such as particulate or fibrous fillers, as described above.

In addition to, or instead of, increasing the Young's modulus to improve dead-fold, the treated sheets may be optionally processed to increase the "bulk hand feel" of a sheet, which is done by disrupting the generally planar nature of the sheet. This can be done, for example, by embossing, crimping, quilting or otherwise texturing the sheet so as to have regularly spaced-apart or random hills and valleys rather than simply a smooth, planar sheet. This may be done, for example, by passing the sheet through a pair of knurled or other embossing-type rollers. Such texturing increases the ability of a sheet to take and maintain a fold, crinkle, creases or other bend, thus improving the dead-fold properties of the sheet.

Another way to increase the surface area of the treated sheets according to the invention so as to increase their bulk hand feel and/or dead-fold is to include particulate fillers in which at least a portion of the particles have a particle size diameter that equals or exceeds the thickness of the polymer coating. In this way, treated sheets can be manufactured that have dead-fold approaching or equaling 100%, which exceeds the dead-fold properties of virtually all conventional paper or plastic wraps and sheets currently on the market. An example of a conventional sheet or wrap having 100% dead-fold is aluminum or other metal foils.

Other properties that may be desirable when manufacturing food wraps are heat resistance, microwaveability, and insulation ability. Increasing the amount of inorganic filler within the polymer blend or composition used to coat or impregnate a fibrous sheet tends to increase the heat resistance, microwaveability, and insulation ability of the treated fibrous sheets. It has been found, for example, that a soft biodegradable polymer can be blended with an inorganic filler, such as ground or precipitated silica, to yield

abiodegradable polymer composition that includes at least about 30% by weight of the inorganic filler. Adding at least about 30% by weight inorganic filler to a soft biodegradable polymer yields a treated fibrous sheet that does not break down when placed in a microwave oven.

The use of fillers, coupled with specific processing techniques, can also be used to create "cavitation". Cavitation occurs as the thermoplastic polymer fraction is pulled in either a monoaxial or biaxial direction and the filler particles create a discontinuity in the film or sheet that increases in size during stretching. During stretching, a portion of the stretched polymer pulls away from the filler particles, resulting in tiny cavities in the vicinity of the filler particles. This, in turn, results in greatly increased breathability and vapor transmission of the sheets and films. It also results in films or sheets having a touch and feel that much more closely resembles the touch and feel of paper, as contrasted with conventional plastic sheets and films. The result is a sheet, film or wrap that can be used for applications that are presently performed or satisfied using paper products (*i.e.,* wraps, tissues, printed materials, etc.)

Treated sheets according to the invention can have any desired thickness. Treated sheets suitable for wrapping, enclosing or otherwise covering food items or other solid substrates will typically have a measured thickness between about 0.0003" and about 0.01" (about 7.5-250 microns), and a calculated thickness between about 0.00015" and about 0.005" (about 4-125 microns).

The measured thickness will typically be between 10-100% larger than the calculated thickness when the sheets and films are made from compositions that have a relatively high concentration of particulate filler particles, which can protrude from the surface of the treated sheet. This phenomenon is especially pronounced when significant quantities of filler particles having a particle size diameter that is larger than the thickness of the polymer matrix are used.

Treated sheets suitable for use as wraps will preferably have a measured thickness in a range from about 0.0004" to about 0.005" (about 10 to about 125 microns), more preferably in a range from about 0.0005" to about 0.003" (about 12 to about 75 microns), and most preferably in a range from about 0.001" to about 0.002" (about 25 to about 50 microns). On the other hand, treated sheets suitable for use as wraps will preferably have a calculated thickness in a range from about 0.0002" to about 0.003" (about 5 to about 75 microns), more preferably in a range from about 0.0003" to about 0.002" (about 7.5 to

about 50 microns), and most preferably in a range from about 0.0005" to about 0.0015" (about 12 to about 40 microns).

The difference between the calculated and measured thickness tends to increase with increasing filler content and also with increasing particle size. Conversely, the difference between the calculated and measured thickness tends to decrease with decreasing filler content and also with decreasing particle size. Treated sheets that include no fillers, or lower quantities of fillers having a particle size diameter that is substantially lower than the thickness of the polymer matrix, will have a measured thickness that is similar or equal to the calculated thickness.

Another important property of the biodegradable blends is that when such blends are used to coat or impregnate fibrous sheets, the treated sheets are readily printable without further processing. Thus, another advantage of utilizing the inventive polymer blends in the manufacture of wraps is that such blends are generally able to accept and retain print much more easily than conventional plastics or waxed papers. Many plastics and waxes are highly hydrophobic and must be surface oxidized in order to provide a chemically receptive surface to which ink can adhere. Biodegradable polymers, on the other hand, typically include oxygen-containing moieties, such as ester or amide groups, to which inks can readily adhere.

### 3. Measuring Dead-Fold

The term "dead-fold" refers to the tendency of a sheet to maintain a crease, crinkle, fold or other bend. The dead-fold properties of a sheet can be accurately measured using a standard test known in the art. This test provides the ability to compare and contrast the dead-fold properties of various sheets. The following equipment is useful in performing the standard dead-fold test: (1) a semicircular protractor, divided along a 1" diameter semicircle; (2) a weight consisting of a smooth-faced metal block that is 0.75" ± 0.05" by 1.25" ± 0.05" and of such a thickness so as to weigh 50 g ± 0.05 g; (3) a 1" x 4" template for cutting test specimens; (4) a timer or stopwatch capable of timing to 1 second; (5) a utility knife or other cutting tool; and (6) a humidity chamber.

The first step is preparation of an appropriately sized sample. In the case where a sheet has different properties in the machine direction compared to the cross-machine direction it may be useful to measure and average the dead-fold properties in both directions. The standard sample specimen is a 1" x 4" strip of the sheet to be tested.

The second step is a conditioning step in order to ensure uniformity of test conditions. The specimens are conditioned by placing them in a humidity chamber at 23 C and 50% relative humidity for a minimum of 24 hours.

The third step is the actual dead-fold test of each conditioned test strip. The specimen is removed from the humidity chamber and its weight recorded. A light mark is made 1" from one end of the test strip. The test strip is then placed on a flat surface and bent over at the mark but without creasing the strip. Next, the weight is placed squarely and gently over the bend with two thirds (or 0.5") of the weight overlapping the specimen so that a crease is formed, and with one third or (0.25") of the weight overhanging the crease. The edges of the weight parallel to the strip should project evenly (about 0.125") beyond each side of the strip. The weight is allowed to rest on the specimen for 10 seconds. Then it is removed. After exactly 30 seconds, the angle formed by the crease is measured.

The foregoing process is repeated using the other side of the strip and using as many additional strips as will give a statistically accurate measure of the dead-fold properties of a given sheet or film. The average angle A is then input into the following formula to determine the percentage dead-fold C for a given sample:

$$C = 100*(180-A)/180$$

If the angle A is 0° (*i.e.*, where the crease is maintained so that no spring back is observed), the sample has 100% dead-fold (C = 100*(180-0)/180 = 100%). At the other extreme, if the angle A is 180° (*i.e.*, where the sample springs all the way back so that the sample is essentially flat, the sample has 0% dead-fold (C = 100*(180-180)/180 = 0%). In the middle, a sample that springs back half way so as to form a right angle has 50% dead-fold (C = 100*(180-90)/180 = 50%).

When used to wrap foods, or whenever good dead-fold properties are desired, treated sheets according to the invention can be manufactured so as to have a dead-fold of at least about 50%. Preferably, treated sheets will have a dead-fold of at least about 60%, more preferably at least about 70%, more especially preferably at least about 80%, and most preferably at least about 90%. Treated sheets according to the invention have been developed that have a dead-fold approaching or equal to 100%. By way of comparison, sheets and films made from polyethylene (*e.g.*, for use in making sandwich or garbage bags) typically have a dead-fold of 0%. Standard paper wraps commonly used in the fast food industry typically have a dead-fold between about 40-80%. Thus, treated sheets according to the invention can be manufactured so as to have dead-fold properties that

meet or exceed those of standard paper wraps, and which are many times greater than conventional plastic films and sheets, often orders of magnitude greater.

## III. METHODS OF MANUFACTURING POLYMER BLENDS AND FIBROUS SHEETS

It is within the scope of the invention to employ any manufacturing apparatus known in the art of manufacturing thermoplastic compositions to form the polymer and any coating apparatus to coat or impregnate fibrous sheets with the polymer blends. Examples of suitable mixing apparatus that can be used to form polymer blends according include a twin-shafted kneader with meshing screws having kneading blocks sold by the Buss Company, a BRABENDER mixer, a THEYSOHN TSK 045 compounder, which is a twin-shaft extruder with shafts rotating in the same direction and which has multiple heating and processing zones, a BUSS KO Kneader having a heatable auger screw, a BAKER-PERKINS MPC/V-30 double and single auger extruder, single or twin auger OMC extruders, a Model EPV 60/36D extruder, a BATTAGGION ME100 direct-current slow mixer, a HAAKE Reomex extruder, a COLLIN Blown Film Extruder, a BATTENFELD-GLOUCESTER Blown Film Extruder, and a BLACK-CLAWSON Cast Film Extruder.

Many of the foregoing mixers are also extruders, which makes them suitable for extruding films or sheets from the polymer blends, which can then be laminated together with a fibrous sheet. Alternatively, polymer blends can be made using transfer-line-injection technology where resin manufacturers can inject the various minor components of these blends into the main poly components during manufacture. One of ordinary skill in the art will be able to select and optimize an appropriate manufacturing apparatus according to the desired article to be manufactured. Once a thermoplastic melt has been formed using any of the above-mentioned mixers, or any other appropriate mixing and melting apparatus known in the thermoplastic art, virtually any molding, extrusion, shaping or coating apparatus known in the thermoplastic molding or processing art can be used to produce finished articles of manufacture comprising fibrous sheets that have been coated or impregnated with a polymer blend to render the sheets more resistant to penetration by liquids.

In a preferred embodiment for manufacturing sheets and films from the polymer blends, which can then be laminated together with fibrous sheets, the sheets and films can be manufactured using a compounding twin screw extruder to prepare the blends, and a blown film or cast film line to make the films and sheets. Blown films and sheets tend to

have similar, if not identical, strength and other performance properties in the biaxial direction due to how they are processed (*i.e.*, they are extruded as a tube and then expanded in all directions by blowing air within the confines of the tube, causing it to expand like a balloon). Cast films or sheets, on the other hand, unless subjected to biaxial stretching, will be substantially stronger (*e.g.* will have substantially greater tensile strength) in the machine direction and will be substantially more tear resistant in the cross-machine direction. When extruding a thermoplastic material, the polymer molecules tend to be oriented in the machine direction. Machine direction orientation is further increased if the extruded sheet or film is passed through a nip to decrease the sheet or film thickness in the machine direction.

The treated sheets according to the invention may be coated or impregnated on one or both sides as desired. They may be formed by laminating a fibrous sheet with one or more sheets or films, co-extruding a sheet or film of a polymer blend with a fibrous sheet, dipping, spreading (*e.g.*, using a doctor blade), spraying, and the like. Because a portion of the treated sheets are thermoplastic, the sheets can be post-treated by heat sealing to join two ends together to form sacks, pockets, pouches, and the like. They can be laminated onto existing sheets or substrates.

Monoaxial or biaxial stretching of sheets and films used to coat a surface of a fibrous sheet can be used to create cavitation. To create cavitation, a particulate filler is included that yields discontinuities as the sheet or film is stretched while still in a thermoplastic condition. Cavitation increases the breathability and vapor transmission of the sheets and films. It also results in films or sheets having a touch and feel that much more closely resembles the touch and feel of paper compared to conventional thermoplastic sheets and films.

When employing certain coating or impregnating techniques, such as spreading or spraying a biodegradable polymer composition onto a fibrous sheet, it may be advantageous to increase the MFI of the molten polymer composition. This allows the molten polymer composition to flow more readily so as to coat or impregnate the fibrous sheet. Preferably, the molten polymer composition has an MFI of at least about 40 g/10 min., more preferably at least about 70 g/10 min., and most preferably at least about 100 g/10 min.

As discussed above, the MFI can, depending on the biodegradable polymer or polymer blend, be increased to a desired level by heating it to a higher temperature. In some cases, however, heating a polymer to temperature that might theoretically decrease

the MFI to an acceptable level might, instead, scorch, burn or otherwise damage the polymer composition. In such cases it may be desirable to add a plasticizer to the polymer composition. The plasticizer might be a volatile or non-volatile plasticizer, as discussed above.

According to one embodiment, water is added to increase the MFI of the molten polymer composition. Adding 200 ppm water to a polymer composition has been found to increase the MFI from 4 g/10 min. to 40 g/10 min. Based on this, one of ordinary skill can adjust the water concentration as desired to raise or lower the MFI to a predetermined level.

In the case of a spray coating method, one or more volatile solvents, such as alcohols, ketones, or chlorinated hydrocarbons, can be used to raise the MFI of the molten polymer composition. During or after the coating process, as the volatile solvent is driven off by evaporation, the solvent is advantageously recovered and reused for both economic and environmental reasons.

## IV. EXAMPLES

The following examples are presented in order to more specifically teach compositions and process conditions for forming biodegradable polymer blends, as well as treated fibrous sheets therefrom. The examples include various mix designs of the inventive biodegradable polymer blends as well various processes for manufacturing the blends and then forming polymeric sheets and films therefrom.

### EXAMPLES 1-3

Biodegradable polymer films were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in terms of weight percent of the entire polymer blend:

| Example | Biomax 6926 | Ecoflex-F | $SiO_2$ |
|---|---|---|---|
| 1 | 94.84% | 5% | 0.16% |
| 2 | 89.84% | 10% | 0.16% |
| 3 | 79.84% | 20% | 0.16% |

The foregoing polymer blends were blended and blown into films at Gemini Plastics, located in Maywood, California, using DuPont supplied BIOMAX 6926 (both new and old lots), a silica master batch in BIOMAX 6926 base resin supplied by DuPont, and ECOFLEX-F resin obtained from BASF. The films were blown using a Gemini film blowing extruder (L/D 24/1) equipped with a 2 inch barrier mixing screw containing a

Maddock shear mixing tip, and a 4 inch diameter annular die with a die gap of 0.032-0.035".

Even though a typical quantity of silica antiblock was used (*i.e.*, 0.16%), significant blocking of the film was observed for the film made using the mix design of Example 3 (*i.e.* 20% ECOFLEX); however, there was no observed blocking of the 5 and 10% ECOFLEX blends of Examples 1 and 2. For purposes of comparison, films of neat ECOFLEX and BIOMAX were manufactured. The neat ECOFLEX films were manufactured using BASF ECOFLEX-F resin and a 30% talc master batch in the same resin. The neat BIOMAX films (new and old) included 0.16% $SiO_2$, while the neat ECOFLEX films included 4.5% talc. The mechanical properties of the BIOMAX/ECOFLEX blend films and the control BIOMAX and neat ECOFLEX-F films were measured under ambient conditions. The data generated is show graphically in Charts 1-8 depicted in Figures 1-8, respectively.

Chart 1, depicted in Figure 1, is a plot of the strain rate versus percent elongation at break for the various films tested. At 500 mm/min. strain rate, both new and old BIOMAX films displayed poor elongation. The neat ECOFLEX films and all of the films made from the BIOMAX-ECOFLEX blends had significantly better elongations than the neat BIOMAX films at all of the strain rates studied. On the other hand, the 20% ECOFLEX blend of Example 3 exhibited equal or better elongation compared to the neat ECOFLEX films at lower strain rates, even though these films included nearly 80% BIOMAX, which was shown to have very poor elongation.

Chart 2, depicted in Figure 2, is a plot of percent elongation versus percentage of ECOFLEX in the BIOMAX/ECOFLEX blends measured at a fixed strain rate of 500 mm/min. As represented by Chart 2, there was a nearly linear improvement in the percent elongation as the concentration of ECOFLEX was increased. Moreover, the 20% ECOFLEX blend of Example 3 had an elongation as good as the neat ECOFLEX films.

Chart 3, depicted in Figure 3, similarly plots the percent elongation versus the percentage of ECOFLEX in the BIOMAX/ECOFLEX blends measured at a fixed strain rate of 1000 mm/min. Again, a dramatic improvement in the elongation of the BIOMAX/ECOFLEX blend was seen as the concentration of ECOFLEX reached 10 and 20%, respectively, although the trend was not as clear as the data in Chart 2, measured at a fixed strain rate of 500 mm/min.

Chart 4, depicted in Figure 4, is a plot of the strain rate versus break stress of the various films. Again, neat ECOFLEX and all of the BIOMAX/ECOFLEX blends had

significantly better break stress than the neat BIOMAX films at all of the strain rates studied. Moreover, the BIOMAX/ECOFLEX blends had significantly better break stress than the neat ECOFLEX films at all strain rates, thus showing that the BIOMAX/ECOFLEX blends are all stronger in tensile strength than either of neat BIOMAX or ECOFLEX.

Chart 5, depicted in Figure 5, is a plot of the break stress versus percent ECOFLEX in the BIOMAX/ECOFLEX blends of Examples 1-3 measured at a fixed strain rate of 500 mm/min. Once again, a nearly linear increase in break stress was observed as the concentration of ECOFLEX was increased. Moreover, the 20% blend of Example 3 exhibited the surprising and unexpected result of having nearly twice the break stress as the neat ECOFLEX film, and nearly three times the break stress as the neat BIOMAX film.

Chart 6, depicted in Figure 6, is a plot of the break stress versus percent ECOFLEX in the BIOMAX/ECOFLEX blends of Examples 1-3 measured at a fixed strain rate of 1000 mm/min. At this strain rate, the 10% ECOFLEX blend of Example 2 had the highest break stress, with a maximum peak stress of 72 MPa.

Charts 7 and 8, depicted in Figures 7 and 8, respectively, plot the water vapor permeability coefficient (WVPC) of the various films as a function of the concentration of ECOFLEX within the films. In Chart 7, the estimated trend line is based on a WVPC of $7.79 \times 10^{-3}$ g $cm/m^2/d/mm$ Hg, which is the lowest measured WVPC for a neat ECOFLEX film. In Chart 8, the estimated trend line is alternatively based on a WVPC of $42 \times 10^{-3}$ g $cm/m^2/d/mm$ Hg, which is the highest measured WVPC for a neat ECOFLEX film. The data in Charts 7 and 8 indicate that the water vapor barrier properties of the 5 and 10% ECOFLEX blends of Examples 1 and 2 were essentially the same as that of the neat BIOMAX film. The WVPC data for all samples were measured by the standard procedures described in the Test Method ASTM F 1249-90.

Chart 9, depicted in Figure 9, is a plot of the modulus of various films as a function of the concentration of ECOFLEX within the films. Surprisingly, the modulus of blends containing BIOMAX and ECOFLEX are significantly higher than of neat BIOMAX and ECOFLEX. Because one of the uses of the films manufactured according to the present invention is as a wrap having good dead-fold properties, and because the degree of dead-fold is believed to be related to the modulus of a film, blends of BIOMAX and ECOFLEX appear to have superior dead-fold properties over each of the neat

BIOMAX and ECOFLEX films, with the 5% and 10% blends exhibiting the highest modulus.

The foregoing films are used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 lb/3000 $ft^2$ tissue paper, to yield a treated sheet. The treated sheet can be used as a food packaging wrap that resists penetration by water and oils found in food.

EXAMPLES 4-5

Films were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in terms of weight percent of the entire polymer blends:

| Example | Biomax 6926 | Ecoflex-F | Talc |
|---|---|---|---|
| 4 | 79.7% | 16.7% | 3.6% |
| 5 | 76.7% | 16.7% | 6.6% |

The films were blown using a Gemini film blowing extruder (L/D 24/1) equipped with a 2 inch barrier mixing screw containing a Maddock shear mixing tip, and a 4 inch diameter annular die with a die gap of 0.032-0.035". The film of Example 5 had better dead-fold properties than the film of Example 4, which might be attributable to the higher concentration of talc within the blend used in Example 5.

The foregoing films are used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 lb/3000 $ft^2$ tissue paper, to yield a treated sheet. The treated sheet can be used as a food packaging wrap that resist penetration by water and oils found in food.

EXAMPLE 6

A film was manufactured from a biodegradable polymer blend having the following mix design, with the concentration being expressed in terms of weight percent of the entire polymer blend:

| | |
|---|---|
| ECOFLEX-F | 20% |
| Thermoplastic Starch | 50% |
| Polylactic Acid | 15% |
| Inorganic Filler | 15% |

The Thermoplastic Starch was obtained from Biotec Biologische Natuverpackungen GmbH & Co., KG ("Biotec"), located in Emmerich, Germany. The polylactic acid was obtained from Cargill-Dow Polymers, LLC, located in Midland,

Michigan, USA. The inorganic filler was calcium carbonate obtained from OMYA, division Pluess-Staufer AG, located in Oftringen, Switzerland.

The foregoing blend was manufactured and blown into films using a proprietary extrusion line thermoplastic starch extrusion/film blowing apparatus manufactured and assembled specifically for Biotec. In particular, the extrusion/film blowing apparatus was manufactured by Dr. Collin GmbH, located in Ebersberg, Germany. A detailed description of an extrusion/film blowing apparatus similar to the one used by Biotec is set forth in U.S. Patent No. 5,525,281 to Lörcks et al. U.S. Patent No. 6,136,097 to Lörcks et al. discloses processes for manufacturing intermediate thermoplastic starch-containing granulates that can be further processed to make films and sheets. For purposes of disclosure, the foregoing patents are incorporated herein by reference.

The film had a modulus of 215.65 MPa. Thus, it had excellent dead-fold properties as a result of the inclusion of the inorganic filler and the polylactic acid, which is a generally stiff, crystalline polymer at room temperature. As set forth above, PLA has a glass transition temperature between 50-60°C. The ECOFLEX and thermoplastic starch (TPS) both acted as soft, low glass transition temperature polymers. The TPS, when blended with additional polymers and at very low water, has a glass transition temperature approaching −60°C. The ECOFLEX and TPS thus assisted the blowability and flexibility of the blend. The TPS also increased the natural polymer content, thus making the film more biodegradable.

The foregoing film is used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 lb/3000 $ft^2$ tissue paper, to yield a treated sheet. The treated sheet can be used as a food packaging wrap that resists penetration by water and oils found in food.

EXAMPLE 7

A film was manufactured from a biodegradable polymer blend having the following mix design, with the concentration being expressed in terms of weight percent of the entire polymer blend:

| | |
|---|---|
| Thermoplastic Starch | 30% |
| BAK 1095 | 60% |
| Inorganic Filler | 10% |

The thermoplastic starch was obtained from Biotec. The BAK 1095 was obtained from Bayer AG, located in Köln, Germany, and was an aliphatic-aromatic

polyesteramide. The inorganic filler was calcium carbonate obtained from OMYA, division Pluess-Staufer AG, located in Oftringen, Switzerland.

The foregoing blend was manufactured and blown into films using the proprietary thermoplastic starch extrusion/film blowing apparatus described in Example 6. The film had excellent dead-fold properties as a result of the inclusion of the inorganic filler and the BAK 1095, which is a somewhat stiff, crystalline polymer at room temperature even though it is classified as "film grade". As set forth above, BAK 1095 behaves as if it has a glass transition temperature of at least 10°C. Because the glass transition temperature of BAK 1095 is relatively low compared to PLA, considerably more BAK could be included without destroying the film-blowing properties and flexibility of the resulting film. The TPS acted as the soft, low glass transition temperature polymer, and further assisted the blowability and flexibility of the blend. It also increased the natural polymer content, thus making the film more biodegradable.

The foregoing film is used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 lb/3000 $ft^2$ tissue paper, to yield a treated sheet. The treated sheet can be used as a food packaging wrap that resists penetration by water and oils found in food.

EXAMPLES 8-12

Films were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in term of weight percent of the entire polymer blend:

| Example | Biomax 6926 | Ecoflex F | Talc | $TiO_2$ | $CaCO_3$ |
|---|---|---|---|---|---|
| 8 | 76% | 15% | 4.5% | 4.5% | -- |
| 9 | 85.5% | 9.5% | -- | 5% | -- |
| 10 | 70% | 17.5% | -- | 2.5% | 10% |
| 11 | 66% | 16.5% | -- | 2.5% | 15% |
| 12 | 58% | 24% | -- | 3% | 15% |

The talc was supplied by Luzenac, located in Englewood, Colorado, having a particle size of 3.8 microns. The titanium dioxide was supplied by Kerr-McGee Chemical, LLC, located in Oklahoma City, Oklahoma, grade TRONOX 470, having a particle size of 0.17 micron. The calcium carbonate was supplied by Omnia, located in Lucerne Valley, California, particle size of 2 microns. The foregoing blends were

manufactured on a Werner Pfeiderer ZSK twin-screw extruder, and blown into sheets using a Gemini film blowing extruder (L/D 24/1) equipped with a 2 inch barrier mixing screw containing a Maddock shear mixing tip, and a 4 inch diameter die. All of the films had excellent dead-fold properties. The polymer blends of Examples 10-12 were also extruded into sheets using a single screw extruder and a 14 inch flat cast-film die, and the usual nip-rolls and film take-up assembly normal to such a system. All of these films also had excellent dead-fold properties.

The foregoing films are used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 lb/3000 $ft^2$ tissue paper, to yield a treated sheet. The treated sheet can be used as a food packaging wrap that resists penetration by water and oils found in food.

Examples 13-61

Blown and cast films and sheets were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in term of weight percent of the entire polymer blend:

| Example | PLA | Biomax | Ecoflex BX 7000 | Eastar Bio Ultra | Eastar Bio GP | $CaCO_3$ | $TiO_2$ | Starch |
|---|---|---|---|---|---|---|---|---|
| 13 | 30% | 0% | 45% | 0% | 8.25% | 14.5% | 2.25% | 0% |
| 14 | 30% | 0% | 30% | 0% | 13.2% | 23.2% | 3.6% | 0% |
| 15 | 30% | 0% | 25% | 0% | 11.55% | 20.3% | 3.15% | 10% |
| 16 | 50% | 0% | 25% | 0% | 8.25% | 14.5% | 2.25% | 0% |
| 17 | 50% | 0% | 10% | 0% | 13.2% | 23.2% | 3.6% | 0% |
| 18 | 50% | 0% | 5% | 0% | 11.55% | 20.3% | 3.15% | 10% |
| 19 | 50% | 0% | 0% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 20 | 50% | 0% | 0% | 0% | 13.2% | 23.2% | 3.6% | 10% |
| 21 | 50% | 0% | 0% | 0% | 11.55% | 20.3% | 3.2% | 15% |
| 22 | 50% | 0% | 0% | 0% | 9.9% | 17.4% | 2.7% | 20% |
| 23 | 50% | 0% | 0% | 0% | 8.25% | 14.5% | 2.25% | 25% |
| 24 | 27% | 0% | 64% | 0% | 2.97% | 5.22% | 0.81% | 0% |
| 25 | 25% | 0% | 58% | 0% | 5.61% | 9.86% | 1.53% | 0% |
| 26 | 23% | 0% | 54% | 0% | 7.59% | 13.34% | 2.07% | 0% |
| 27 | 30% | 0% | 40% | 0% | 0% | 0.0% | 0.0% | 30% |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 28 | 15% | 0% | 60% | 0% | 0% | 0.0% | 0.0% | 25% |
| 29 | 25% | 0% | 25% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 30 | 20% | 0% | 20% | 0% | 19.8% | 34.8% | 5.4% | 0% |
| 31 | 35% | 0% | 5% | 0% | 19.8% | 34.8% | 5.4% | 0% |
| 32 | 40% | 0% | 10% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 33 | 50% | 0% | 0% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 34 | 20% | 0% | 0% | 20% | 19.8% | 34.8% | 5.4% | 0% |
| 35 | 27% | 0% | 36% | 0% | 3.3% | 5.8% | 0.9% | 27% |
| 36 | 21% | 0% | 28% | 0% | 9.9% | 17.4% | 2.7% | 21% |
| 37 | 28.5 % | 0% | 38% | 5% | 0% | 0% | 0% | 28.5% |
| 38 | 40% | 0% | 0% | 7% | 16.5% | 29.0% | 4.5% | 3% |
| 39 | 40% | 0% | 7% | 0% | 16.5% | 29.0% | 4.5% | 3% |
| 40 | 50% | 0% | 0% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 41 | 20% | 0% | 0% | 20% | 19.8% | 34.8% | 5.4% | 0% |
| 42 | 30% | 0% | 0% | 14% | 16.5% | 29.0% | 4.5% | 6% |
| 43 | 40% | 0% | 0% | 14% | 13.2% | 23.2% | 3.6% | 6% |
| 44 | 0% | 40% | 0% | 14% | 13.2% | 23.2% | 3.6% | 6% |
| 45 | 0% | 50% | 0% | 0% | 16.5% | 29.0% | 4.5% | 0% |
| 46 | 0% | 45% | 0% | 0% | 18.15% | 31.9% | 4.95% | 0% |
| 47 | 0% | 40% | 0% | 0% | 19.8% | 34.8% | 5.4% | 0% |
| 48 | 0% | 40% | 0% | 0% | 19.8% | 34.8% | 5.4% | 0% |
| 49 | 40% | 0% | 14% | 0% | 13.2% | 23.2% | 3.6% | 6% |
| 50 | 0% | 30% | 0% | 7% | 19.8% | 34.8% | 5.4% | 3% |
| 51 | 0% | 35% | 0% | 7% | 18.15% | 31.9% | 4.95% | 3% |
| 52 | 0% | 38% | 0% | 1.4% | 19.8% | 34.8% | 5.4% | 0.6% |
| 53 | 0% | 35% | 0% | 3.5% | 19.8% | 34.8% | 5.4% | 1.5% |
| 54 | 40% | 0% | 0% | 14% | 13.2% | 23.2% | 3.6% | 6% |
| 55 | 40% | 0% | 0% | 0% | 26.7% | 22.7% | 3.5% | 7.1% |
| 56 | 40% | 0% | 0% | 13.8% | 12.9% | 22.7% | 3.5% | 7.1% |
| 57 | 40% | 0% | 0% | 26.7% | 0% | 22.7% | 3.5% | 7.1% |
| 58 | 40% | 0% | 0% | 13.8% | 12.9% | 22.7% | 3.5% | 7.1% |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 59 | 40% | 0% | 0% | 0% | 26.7% | 22.7% | 3.5% | 7.1% |
| 60 | 40% | 0% | 0% | 14% | 13.2% | 23.2% | 3.6% | 6% |
| 61 | 0% | 50% | 0% | 0% | 16.5% | 29.0% | 4.5% | 0% |

The compositions of Examples 13-59 were all processed and blown into films using a COLLIN Blown Film Extruder. The films made using the compositions of Examples 30-34, 36, 38, 41 and 43 were tested and found to have dead-folds of 100%, 92%, 92%, 91%, 100%, 100%, 100%, 100% and 100%, respectively. Although films made from the other compositions were not tested for dead-fold, they would be expected to have relatively high dead-fold compared to conventional biopolymers (*i.e.*, at least about 80%). The water vapor transmission rate for films made using the compositions of Examples 36, 38, 41 and 43 were 91.94, 91.32, 98.29 and 80.31 $g/m^2/day$, respectively.

The composition of Example 60 was processed and blown into a film using a BATTENFELD-GLOUCESTER Blown Film Extruder. A film made from this composition was found to have a water vapor transmission rate of 42.48 $g/m^2/day$.

The composition of Example 61 was processed and blown into various films using both a BATTENFELD-GLOUCESTER Blown Film Extruder and a BLACK-CLAWSON Cast Film Extruder. The film formed using the BATTENFELD-GLOUCESTER Blown Film Extruder apparatus was tested and found to have a dead-fold of 100%. Two different thicknesses of films were formed using the BLACK-CLAWSON Cast Film Extruder, one having a thickness of 1.3 mils (0.0013") and another having a thickness of 1.8 mils (0.0018"). Both had a distinctive machine direction orientation because they were cast, rather than blown, films. The 1.3 mil film had a dead-fold of 99%, and the 1.8 mil film had a dead-fold of 100%.

The foregoing films and sheets are used to laminate at least one side of a fibrous sheet, such as a tissue paper, more particularly a 12-15 $lb/3000\ ft^2$ tissue paper, to yield a treated film or sheet. The treated film or sheet can be used as a food packaging wrap that resists penetration by water and oils found in food.

EXAMPLE 62

Any of the foregoing biodegradable polymer blends is used to coat or impregnate at least one side of a fibrous sheet. The polymer blend is heated, mixed or otherwise processed into a thermoplastic melt and then spread over a surface of a fibrous sheet using a doctor blade. The fibrous sheet is moved while the doctor blade remains

stationary. Alternatively, the polymer blend is sprayed onto the fibrous sheet using spray-coating techniques known in the art.

EXAMPLE 63

Any of the foregoing biodegradable polymer blends is modified by adding silica or replacing some or all of the calcium carbonate with silica. The modified composition is used to coat or impregnate at least one side of a fibrous sheet. The polymer blend is heated, mixed or otherwise processed into a thermoplastic melt and then spread over a surface of a fibrous sheet using a doctor blade. The fibrous sheet is moved while the doctor blade remains stationary. Alternatively, the polymer blend is sprayed onto the fibrous sheet using spray-coating techniques known in the art.

EXAMPLE 64

Any of the foregoing compositions is modified by removing at least a portion of the particulate filler and then using the modified biodegradable composition to coat one or both sides of a fibrous sheet.

The present invention may be embodied in other specific 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. The scope of the invention is, 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.

## CLAIMS

What is claimed is:

1. An article of manufacture comprising:

a fibrous sheet,

at least a portion of the fibrous sheet being coated or impregnated with a biodegradable composition that renders the fibrous sheet more resistant to liquids, the biodegradable composition comprising:

at least one soft thermoplastic biodegradable polymer having a glass transition temperature less than about 0°C.; and

at least one stiff thermoplastic biodegradable polymer having a glass transition temperature of at least about 10°C.

2. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer comprises a modified polyethylene terephthalate in which a portion of the terephthalate groups are substituted with at least one aliphatic diacid.

3. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer comprises at least one of a polyesteramide, a polyhydroxybutyrate having a glass transition temperature of at least about 10°C., a terpolymer including units formed from glycolide, lactide and ε-caprolactone, or a polyesteramide formed from at least one diacid, at least one diol, and at least one amino acid.

4. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer comprises at least one of a polylactic acid or a polylactic acid derivative.

5. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer comprises at least one of an aliphatic polyester including units formed from at least one of a lactide or a hydroxyacid having at least 4 carbon atoms, a polyester including units formed from succinic acid and an aliphatic diol, and at least one aliphatic diol, polycaprolactone, polyhydroxybutyrate-hydroxyvalerate copolymer, polybutylene succinate, polybutylene succinate adipate, polyethylene succinate, or thermoplastic starch.

6. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer comprises at least one of an aliphatic-aromatic copolyester including units formed from an aliphatic diol, an aliphatic diacid and an

aromatic diacid or an aliphatic-aromatic copolyester including units formed from adipic acid, dialkyl terephthalate, and at least one aliphatic diol.

7. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer is included in a range of about 20% to about 99% by weight of the biodegradable composition.

8. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer is included in a concentration of at least about 40% by weight of the biodegradable composition.

9. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer is included in a concentration of at least, but not including, 50% by weight of the biodegradable composition.

10. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer has a glass transition temperature of at least about 15°C.

11. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer has a glass transition temperature of at least about 25°C.

12. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer has a glass transition temperature of at least about 35°C.

13. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer is included in a concentration up to about 70% by weight of the biodegradable composition.

14. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer is included in a concentration up to, but not including, 50% by weight of the biodegradable composition.

15. An article of manufacture as defined in claim 1, wherein the stiff thermoplastic biodegradable polymer is included in a concentration up to about 45% by weight of the biodegradable composition.

16. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer has a glass transition temperature less than about −4°C.

17. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer has a glass transition temperature less than about −10°C.

18. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer has a glass transition temperature less than about −20°C.

19. An article of manufacture as defined in claim 1, wherein the soft thermoplastic biodegradable polymer has a glass transition temperature less than about −30°C.

20. An article of manufacture as defined in claim 1, the biodegradable composition further comprising at least one particulate filler.

21. An article of manufacture as defined in claim 20, the particulate filler being included in an amount so as to render the article of manufacture microwaveable.

22. An article of manufacture as defined in claim 20, the particulate filler being included in an amount of at least about 10% by weight of the biodegradable composition.

23. An article of manufacture as defined in claim 20, the particulate filler being included in an amount of at least about 20% by weight of the biodegradable composition.

24. An article of manufacture as defined in claim 20, the particulate filler being included in an amount of at least about 30% by weight of the biodegradable composition.

25. An article of manufacture as defined in claim 20, the particulate filler comprising at least one of silica, calcium carbonate, clay, talc, mica, alumina, or ceramic.

26. An article of manufacture as defined in claim 1, the biodegradable composition comprising a film or sheet that has been laminated to at least one side of the fibrous sheet.

27. An article of manufacture as defined in claim 1, the fibrous sheet comprising tissue paper, paper or paperboard.

28. An article of manufacture as defined in claim 1, the fibrous sheet comprising 8-60 lb/3000 $ft^2$ paper prior to being coated or impregnated with the biodegradable composition.

29. An article of manufacture as defined in claim 1, the fibrous sheet comprising 12-15 lb/3000 $ft^2$ tissue paper prior to being coated or impregnated with the biodegradable composition.

30. An article of manufacture comprising:

a fibrous sheet,

at least a portion of the fibrous sheet being coated or impregnated with a biodegradable composition that renders the fibrous sheet more resistant to liquids, the biodegradable composition comprising at least one type of polyhydroxybutyrate.

31. An article of manufacture as defined in claim 30, the fibrous sheet comprising tissue paper, paper or paperboard.

32. An article of manufacture as defined in claim 30, the fibrous sheet comprising 12-15 lb/3000 $ft^2$ tissue paper.

33. An article of manufacture as defined in claim 30, the biodegradable composition comprising at least about 30% by weight of an inorganic filler.

34. An article of manufacture as defined in claim 33, the inorganic filler comprising at least one of silica, sand, crushed rock, bauxite, granite, limestone, sandstone, glass beads, aerogel, xerogel, mica, clay, alumina, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, gypsum, insoluble salts, calcium carbonate, magnesium carbonate, calcium aluminate, magnesium carbonate, titanium dioxide, talc, ceramic, zirconium compounds, xonotlite (a crystalline calcium silicate gel), lightweight expanded clay, perlite, vermiculite, pumice, zeolites, minerals, or other geologic material.

35. An article of manufacture comprising:

a fibrous sheet,

at least a portion of the fibrous sheet being coated or impregnated with a biodegradable composition that renders the fibrous sheet more resistant to liquids, the biodegradable composition comprising:

at least biodegradable polymer; and

at least one inorganic filler included in a concentration of at least about 30% by weight of the biodegradable composition.

36. An article of manufacture as defined in claim 35, wherein the biodegradable composition comprises at least one soft biodegradable polymer having a glass transition temperature less than about 0° C.

37. An article of manufacture as defined in claim 36, wherein the biodegradable composition further comprises at least one stiff biodegradable polymer having a glass transition temperature of at least about 10° C

38. An article of manufacture as defined in claim 36, wherein the biodegradable composition comprises silica as the inorganic filler.

39. An article of manufacture as defined in claim 38, wherein the article of manufacture is microwaveable.

40. An article of manufacture as defined in claim 35, the fibrous sheet comprising 12-15 lb/3000 $ft^2$ tissue paper.

41. A method of rendering a fibrous sheet more resistant to liquids, comprising:

providing a fibrous sheet; and

coating or impregnating the fibrous sheet with a biodegradable composition in order to render the fibrous sheet more resistant to liquids, the thermoplastic biodegradable composition comprising:

at least one soft thermoplastic biodegradable polymer having a glass transition temperature less than about 0°C.; and

at least one stiff thermoplastic biodegradable polymer having a glass transition temperature of at least about 10°C.

42. A method as defined in claim 41, the method comprising:

heating the thermoplastic biodegradable composition so as to form a thermoplastic melt comprising an initially flowable composition;

applying the thermoplastic melt to at least one side of the fibrous sheet so as to coat or impregnate the fibrous sheet; and

allowing the thermoplastic melt to harden.

43. A method as defined in claim 42, wherein the thermoplastic melt is applied to the at least one side of the fibrous sheet using a doctor blade or by spraying.

44. A method as defined in claim 43, wherein the thermoplastic melt has a melt flow index of at least about 40 g/10 min.

45. A method as defined in claim 43, wherein the thermoplastic melt has a melt flow index of at least about 70 g/10 min.

46. A method as defined in claim 43, wherein the thermoplastic melt has a melt flow index of at least about 100 g/10 min.

47. A method as defined in claim 41, the method comprising:

heating the thermoplastic biodegradable composition so as to form a thermoplastic melt comprising an initially flowable composition;

forming a sheet or film from the thermoplastic melt; and

laminating the sheet or film to at least one side of the fibrous sheet.

48. A method as defined in claim 47, wherein the sheet or film is formed by at least one of casting, extrusion or blowing.

49. A method as defined in claim 48, wherein the sheet or film is laminated to the fibrous sheet by co-extrusion.

50. A method as defined in claim 41, the fibrous sheet comprising tissue paper, paper or paperboard.

51. A method as defined in claim 50, the fibrous sheet comprising 12-15 lb/3000 $ft^2$ tissue paper.

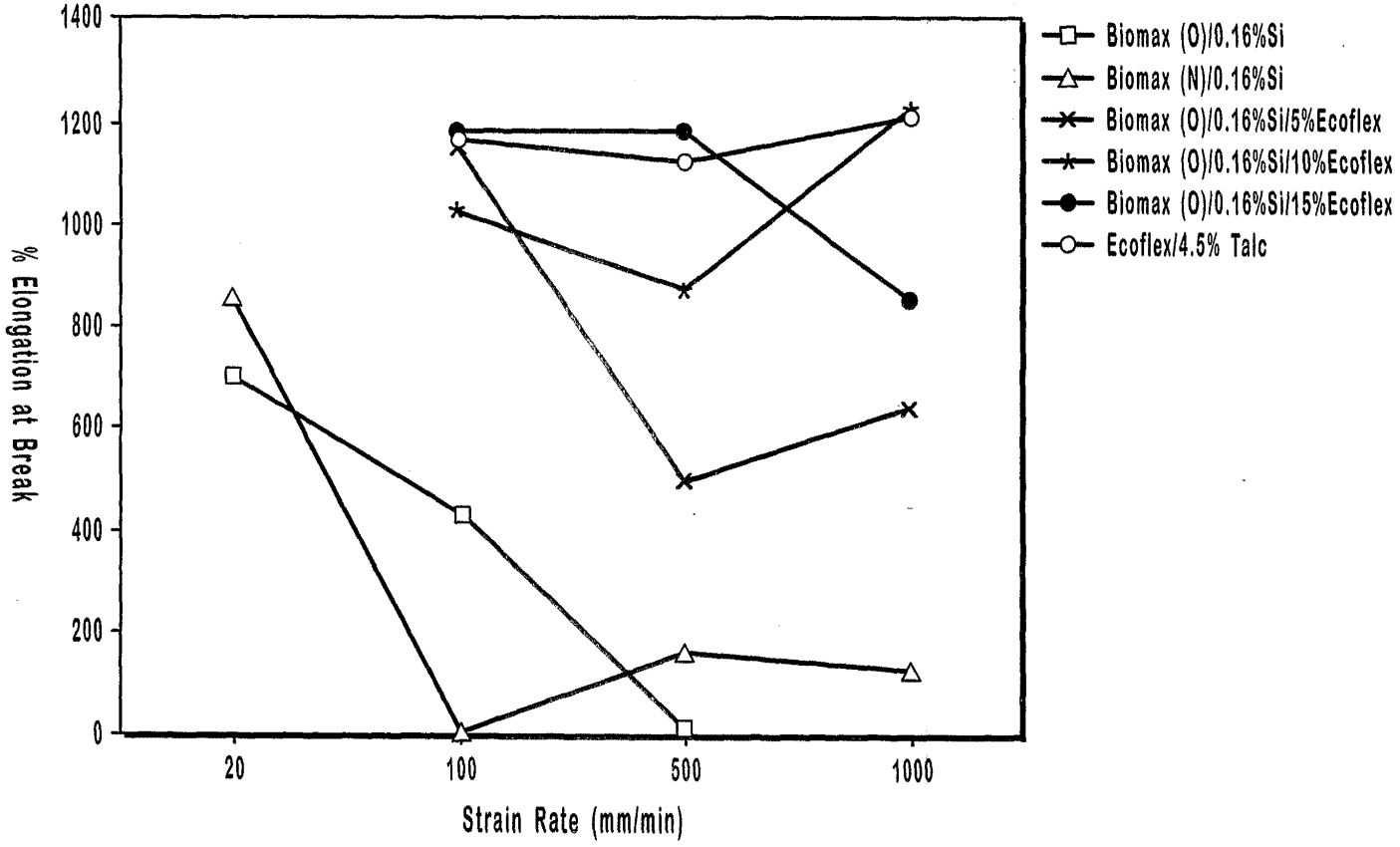



Fig. 1



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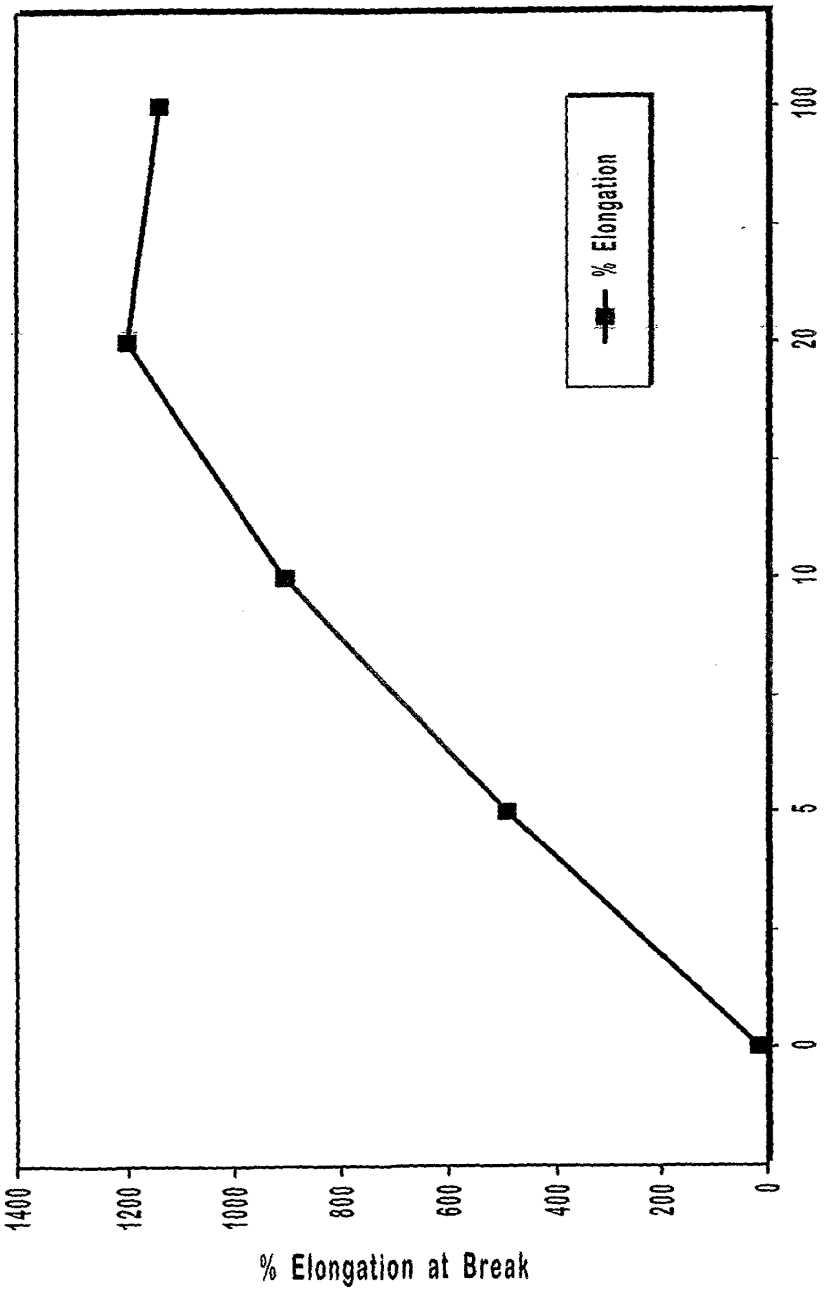

% Elongation
% Elongation at Break
% Ecoflex
0
200
400
600
800
1000
1200
1400
0
5
10
20
100

Fig. 2

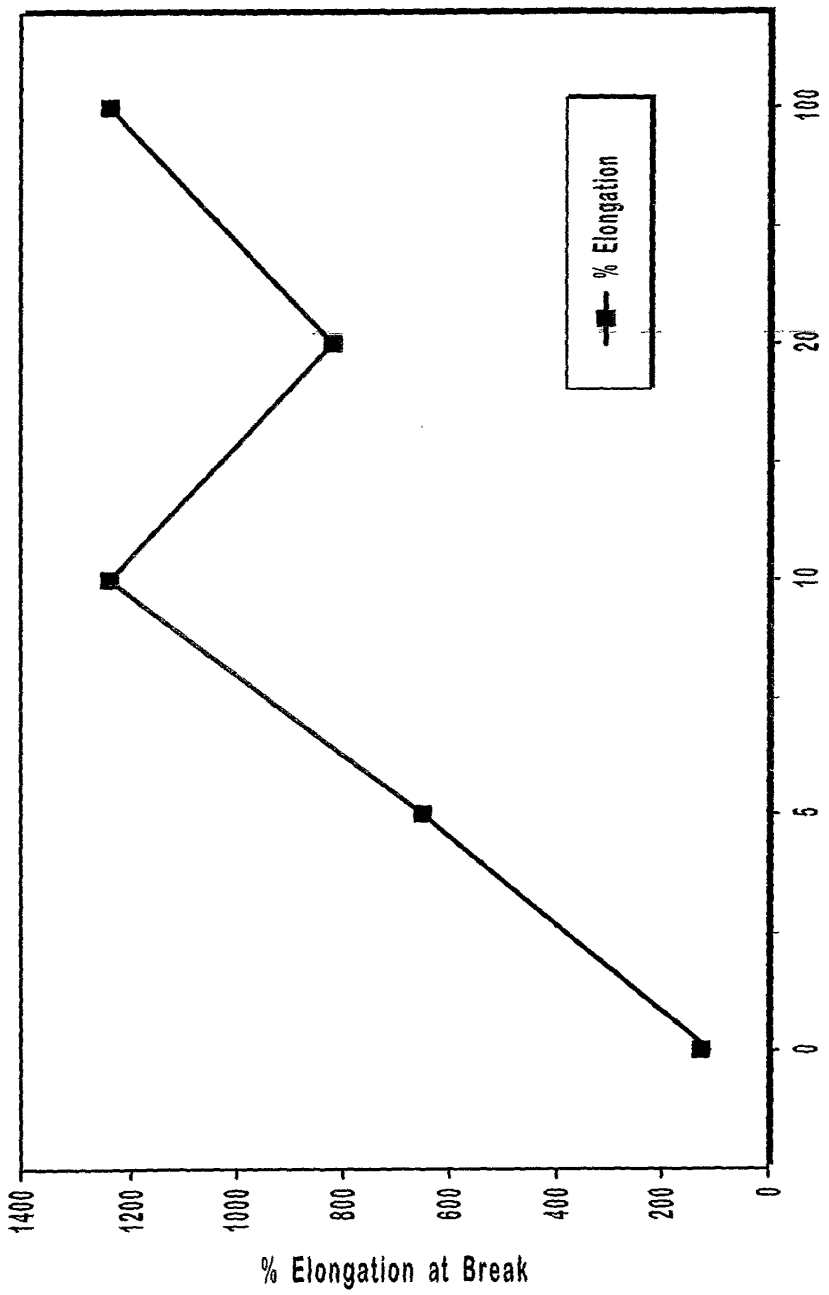

% Elongation
% Elongation at Break
% Ecoflex
1400
1200
1000
800
600
400
200
0
0
5
10
20
100

Fig. 3

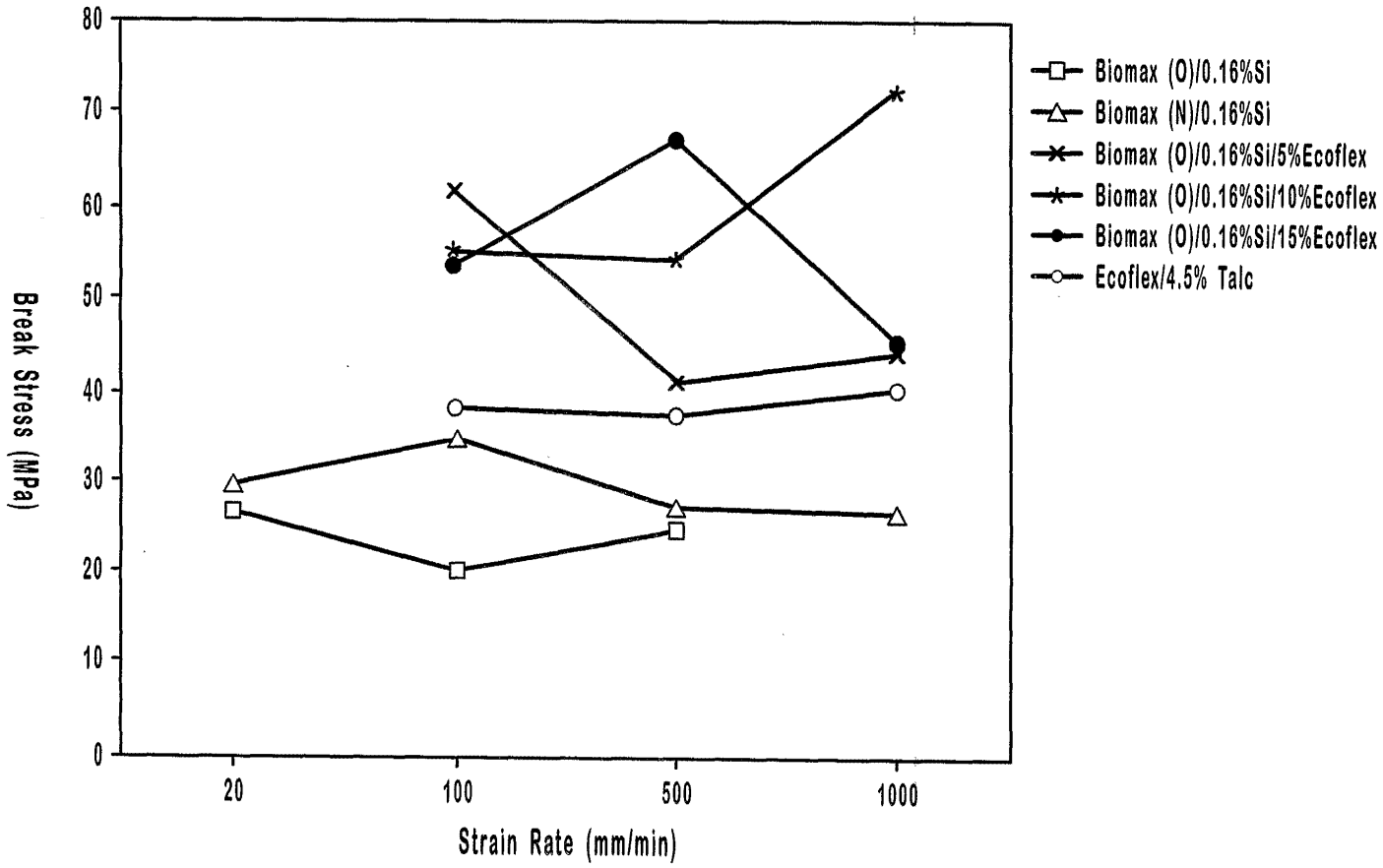



Fig. 4



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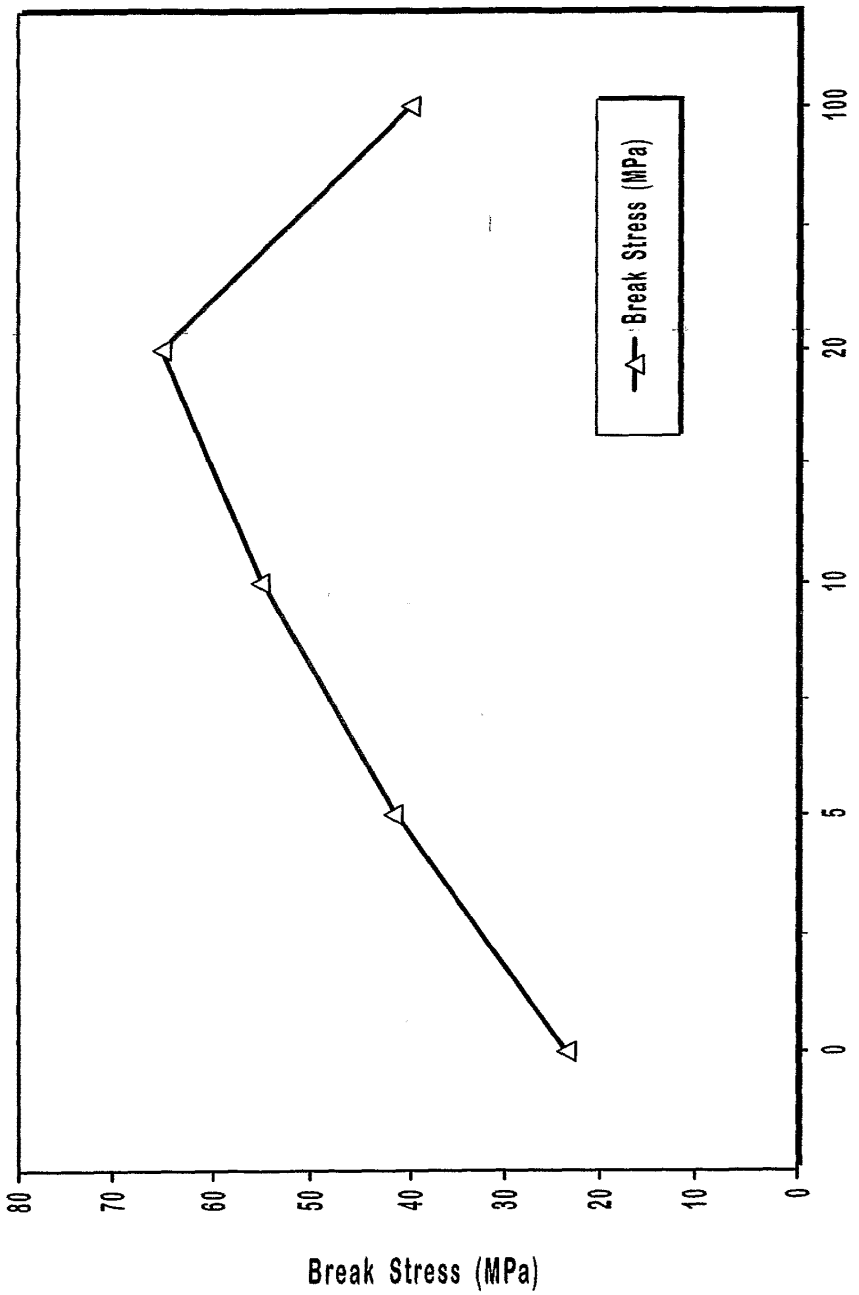

Break Stress (MPa)
80
70
60
50
40
30
20
10
0
Break Stress (MPa)
0
5
10
20
100
% Ecoflex

Fig. 5

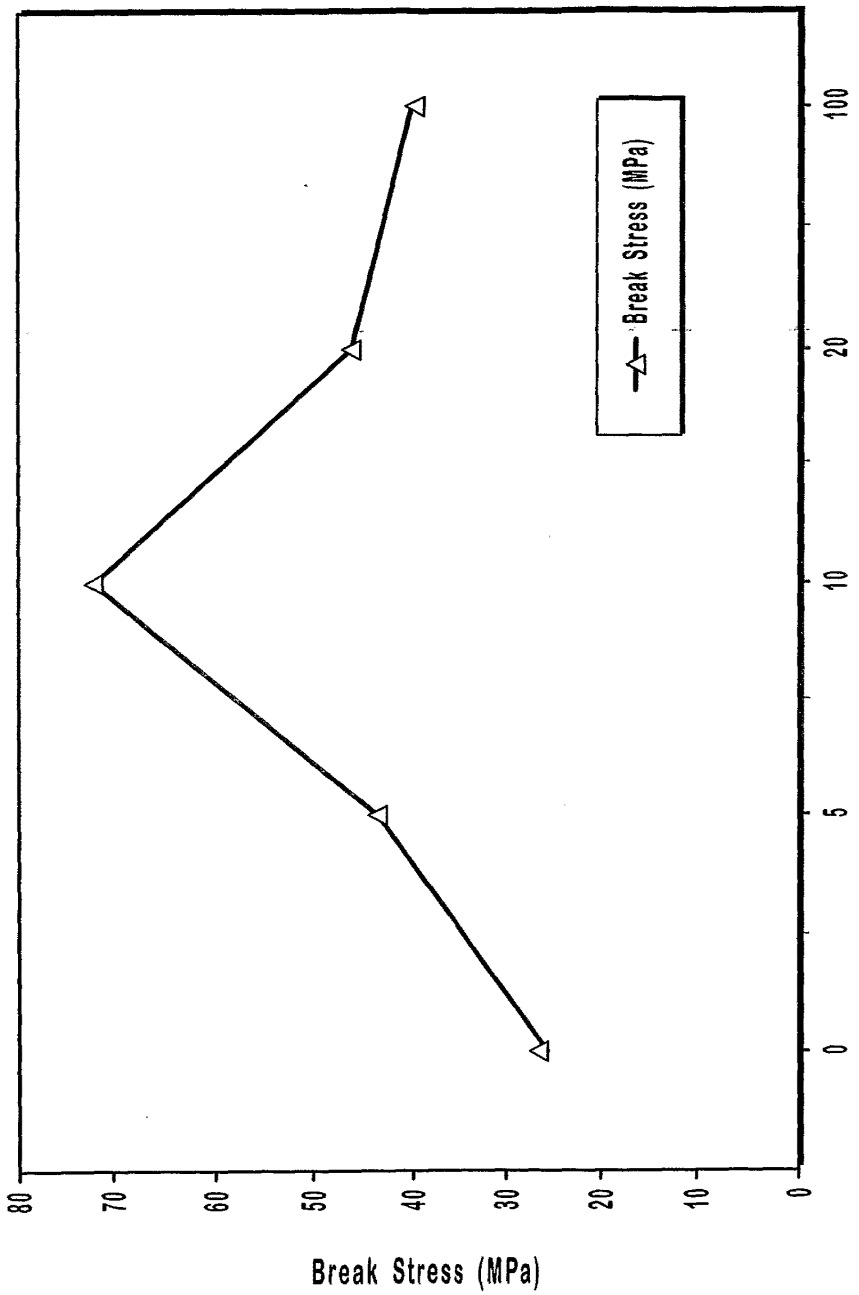

Break Stress (MPa)
80
70
60
50
40
30
20
10
0
Break Stress (MPa)
0
5
10
20
100
% Ecoflex

Fig. 6

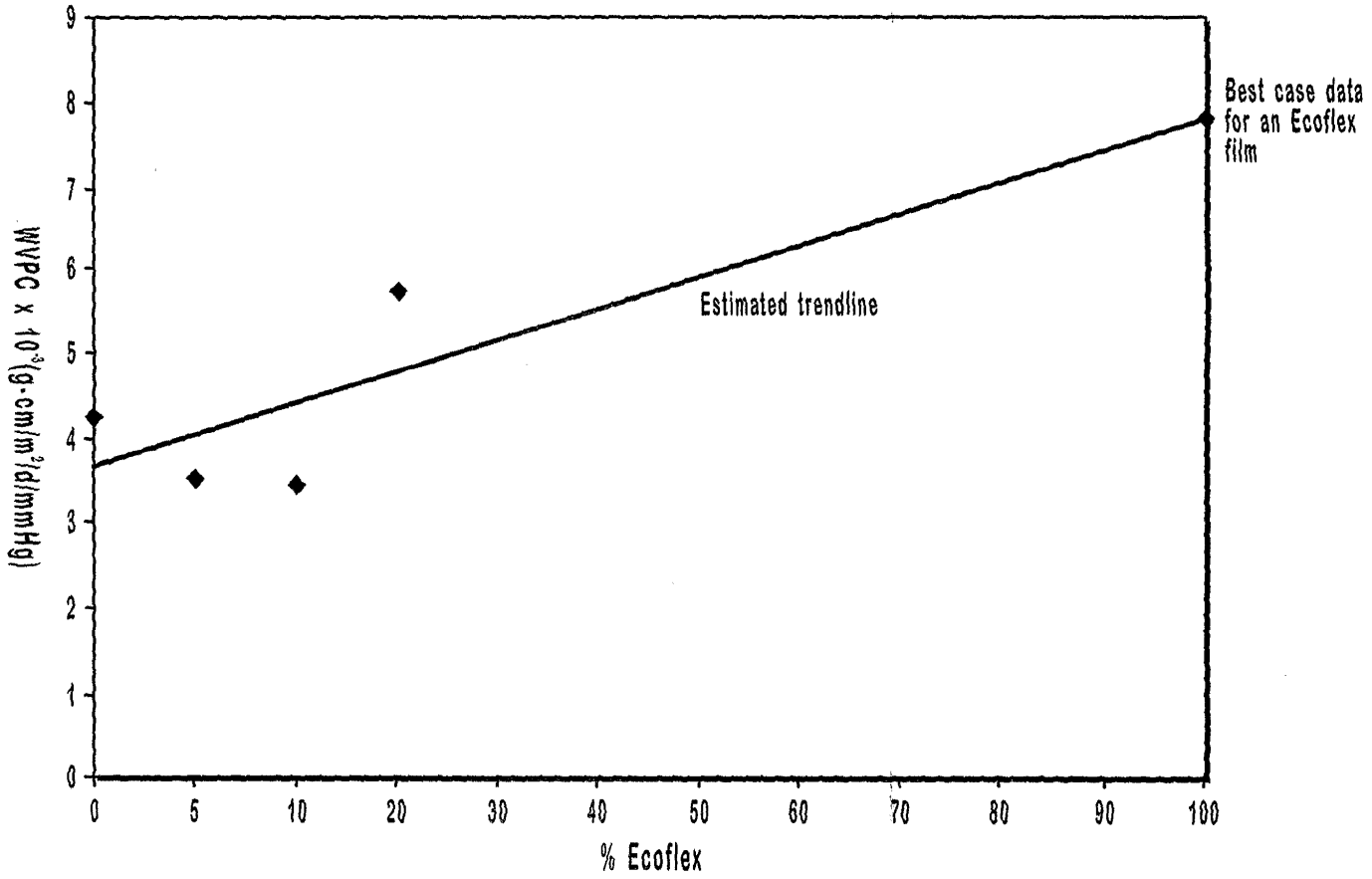



Fig. 7





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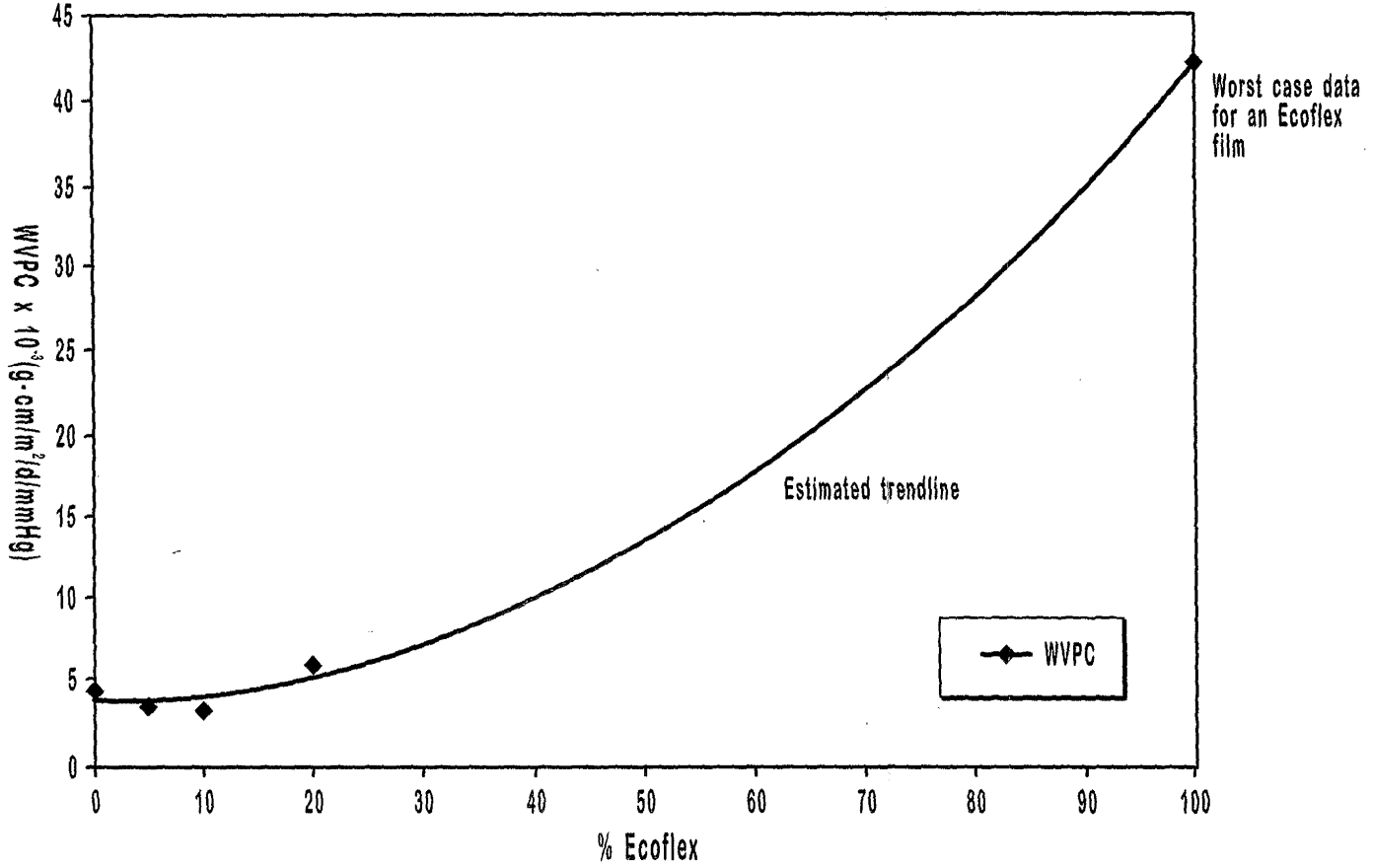



Fig. 8





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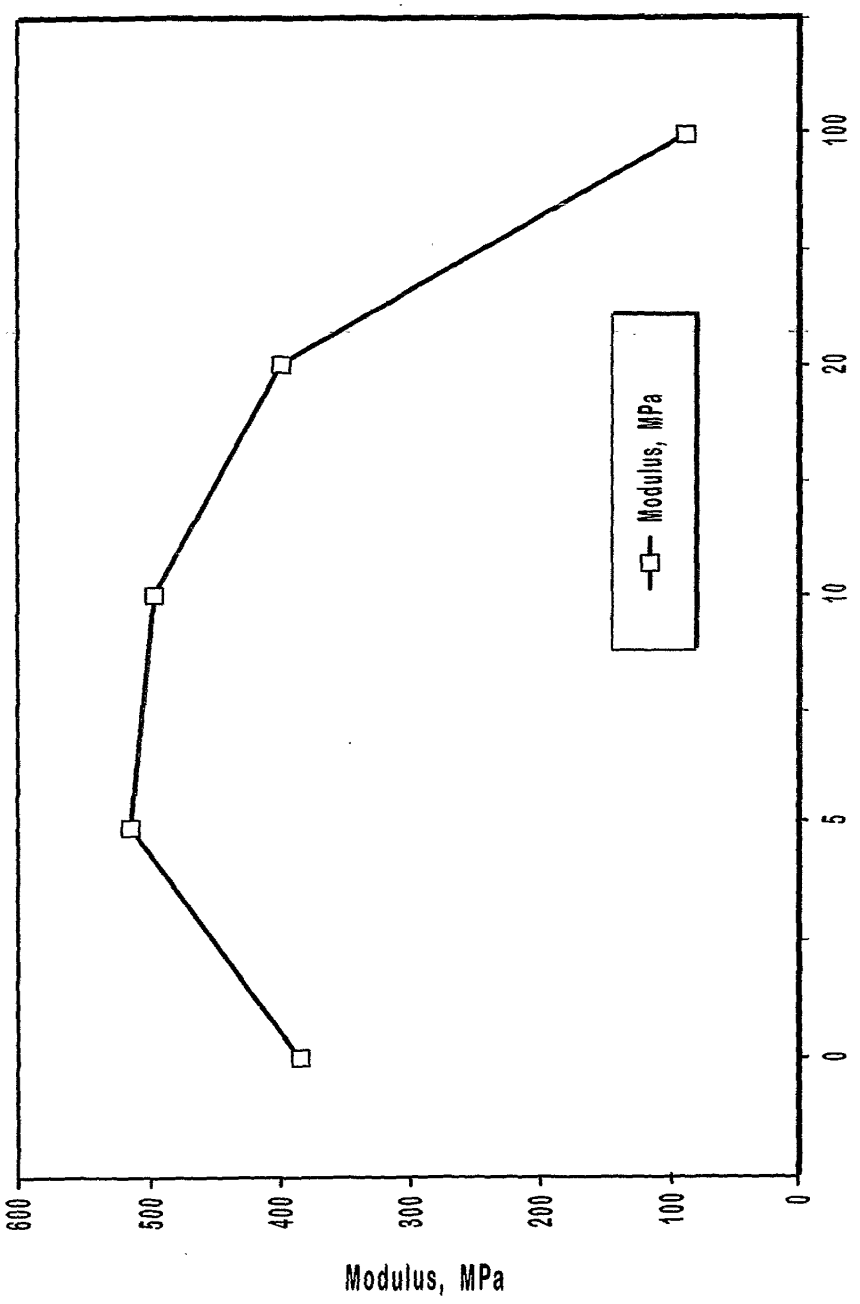

Modulus, MPa
600
500
400
300
200
100
0
Modulus, MPa
0
5
10
20
100
% Ecoflex

Fig. 9

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

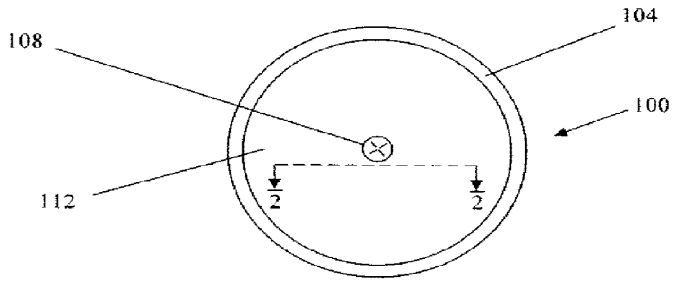
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(54) **Title**: THERMOFORMED ARTICLE MADE FROM BIO-BASED BIODEGRADABLE POLYMER COMPOSITION

FIG. 1




(57) **Abstract**: The present invention provides a biodegradable polymer composition useful for manufacturing biodegradable in which, the process comprising: (1) providing a renewable polymer and/or natural fiber having: (a) a $T_s$ value of up to about 90°C; and (b) a heat distortion index of up to about 90°C; (2) providing a heat-resistant polymer having: (a) a $T_s$ of greater than about 60°C; and (b) a heat distortion index greater than about 50°C, wherein the $T_s$ value and heat distortion index of the heat-resistant polymer is greater than that of the renewable polymer and/or natural fiber; and (3) coextruding the heat-resistant polymer and the renewable polymer to provide a thermoformable composite comprising a core comprising the renewable polymer and/or natural fiber, wherein the renewable polymer and/or natural fiber comprises at least about 50% by weight of the composite and a heat-resistant outer layer comprising the heat-resistant polymer which substantially surrounds the core.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

# THERMOFORMED ARTICLE MADE FROM BIO-BASED BIODEGRADABLE POLYMER COMPOSITION

## RELATED PATENT APPLICATION

This is a non-provisional application which claims priority from U.S. Provisional Patent Application Serial Numbers 61/126,453 and 61/126,452 both filed on May 5, 2008.

## FIELD OF THE INVENTION

The present invention broadly relates to articles comprising a thermoformable composite comprising a core comprising a renewable polymer and a heat-resistant outer layer substantially surrounding the core and comprising a heat-resistant polymer. The present invention also relates to a method for coextruding the heat-resistant polymer outer layer and renewable polymer core to provide the thermoformable composite.

## BACKGROUND OF THE INVENTION

Polylactic acid (PLA) is increasing in favor with consumers of plastic thermoformed articles as a renewable plastic which does not derive from fossil fuels and which is degradable in the environment. As with many thermoplastics, PLA has a decreasing mechanical strength with increasing temperature. At higher temperatures approaching about 140°F (60°C), an article formed from PLA may lose the ability to resist deformation by forces frequently found in transportation. At temperatures above about 140°F (60°C), PLA may lose its ability to resist deformation to forces of the order of magnitude of gravity and residual mold stress. Prolonged exposure of PLA articles to temperatures of about 140°F (60°C) or higher may cause these articles to deform substantially from their original shape under forces which may be present in storage conditions. Since temperatures of about 130°F (54.4°C) may be exceeded in railcars and trailers used for distribution, PLA articles may suffer from high damage losses during transport through and storage in hot areas such as tractor trailer crossing, for example, the sunny warmer portions of the United States during the summer.

Accordingly, it would be desirable to develop bio based, biodegradable polymer compositions comprising poly (lactic acid) and further components of natural origin which

exhibit improved mechanical properties as compared to currently available similar material and make products on the basis of the aforementioned compositions.

## SUMMARY OF THE INVENTION

PLA is a biodegradable polymer that made from corn starch. It has been used to produce a few environment friendly products, such as International Paper's Ecotainer product. The limited thermal and mechanical properties of virgin PLA, however, become the restriction of its applications. Adding petroleum chemicals into PLA could improve the performance, but damaged the sustainability of the products. By making PLA / natural filler composites, we can have better products, while retain their sustainability. The natural fillers here are, but not limit to, cellulose fibers and powders; agriculture (for examples, rice husk, wheat bran, straw, corn cob...) fibers and powders; wood fibers and powders; and bamboo fibers and powders. The products of the present invention are 1) better performance than the pure PLA resin itself, 2) environmentally friendly, and 3) results in lower cost.

In recent years, there has been a marked increase in interest in bio-based and biodegradable materials for use in food packaging, agriculture, medicine, and other areas. For example, the poly (lactic acid) (PLA) made from corn starch has been used to produce a few environment friendly products. However, the limited thermal and mechanical properties of virgin biopolymers have become the restriction of its applications. Petroleum chemicals, for example, PET, polypropylene copolymer, and its copolymer could be added into PLA to improve its performance. By combining biopolymers, and/or biodegradable polymers, and/or natural fillers, and/or performance promoters or modifiers better products can be made with having good sustainability. The Biopolymers are, but not limit to, PLA, PHA (polyhydroxyalkanoates), cellulose esters, polysaccharides, and so on. The natural fillers are, but not limited to, cellulose fibers and powders; agriculture (for examples, rice husk, wheat bran, straw, corn cob...) fibers and powders, wood fibers and powders, bamboo fibers and powders. The performance promoters or modifiers are, but not limited to, low molecule weight compounds, like crosslink agents, plasticizers, stabilizers, and the like.

According to a first broad aspect of the present invention, there is provided an article



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comprising a thermoformable composite comprising:

a core comprising a renewable polymer having: (a) a $T_s$ value of up to about 90°C; and (b) a heat distortion index of up to about 90°C; and

a heat-resistant outer layer substantially surrounding the core and comprising a heat-resistant polymer having: (a) a $T_s$ value of greater than about 60°C; and (b) a heat distortion index of greater than about 50°C;

wherein the renewable polymer comprises at least about 50% by weight of the composite;

wherein the heat-resistant polymer has a $T_s$ value and heat distortion index greater than that of the renewable polymer.

According to a second broad aspect of the present invention, there is provided a method comprising the following steps of:

(1) providing a renewable polymer having: (a) a $T_s$ value of up to about 90°C; and (a) a heat distortion index of up to about 90°C;

(2) providing a heat-resistant polymer having: (a) a $T_s$ of greater than about 60°C; and (b) a heat distortion index greater than about 50°C, wherein the $T_s$ value and heat distortion index of the heat-resistant polymer is greater than that of the renewable polymer; and

(3) coextruding the heat-resistant polymer and the renewable polymer to provide a thermoformable composite comprising:

a core comprising the renewable polymer, wherein the renewable polymer comprises at least about 50% by weight of the composite; and

a heat-resistant outer layer comprising the heat-resistant polymer which substantially surrounds the core.



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## BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in conjunction with the accompanying drawings, in which:

FIG. 1 is a top plan view of an embodiment of an article comprising a thermoformable composite according to the present invention;

FIG. 2 is a sectional view taken along line 2-2 of FIG. 1;

FIG. 3 is a schematic diagram illustrating an embodiment of a method for preparing an article comprising a thermoformable composite according to the present invention;

Fig. 4 is a graph which shows a typical Differential Scanning Calorimetry (DSC) Spectrum of PLA;

Fig. 5 is a graph which shows a Differential Scanning Calorimetry (DSC) Spectra of PLHB120 and PLHE24; and

Fig. 6 is a graph which shows a Differential Scanning Calorimetry (DSC) Spectra of PLHL34 and PLHL89.

## DETAILED DESCRIPTION OF THE INVENTION

It is advantageous to define several terms before describing the invention. It should be appreciated that the following definitions are used throughout this application.

***Definitions***

Where the definition of terms departs from the commonly used meaning of the term, applicant intends to utilize the definitions provides below, unless specifically indicated.

For the purposes of the present invention, the term "renewable polymer" (also known as "biopolymer") refers to a polymer, or a combination (*e.g.*, blend, mixture, *etc.*) of polymers, which may be obtained from renewable natural resources, *e.g.*, from raw or starting materials which are or may be replenished within a few years (versus, for example, petroleum which



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requires thousands or millions of years). For example, a renewable polymer may include a polymer that may be obtained from renewable monomers, polymers which may be obtained from renewable natural sources (*e.g.*, starch, sugars, lipids, corn, sugar beet, wheat, other, starch-rich products *etc.*) by, for example, enzymatic processes, bacterial fermentation, other processes which convert biological materials into a feedstock or into the final renewable polymer, *etc.* See, for example, U.S. Pat. App. No. 20060036062 (Ramakrishna *et al.*), published February 16, 2006, the entire disclosure and contents of which is hereby incorporated by reference. Renewable polymers useful in embodiments of the present invention may include polyhydroxyalkanoate polymers, polycaprolactone (PCL) polymers, starch-based polymers, cellulose-based polymers, *etc.*, or combinations thereof. Renewable polymers may, but do not necessarily include, biodegradable polymers.

For the purposes of the present invention, the term "biodegradable polymer" refers to a polymer which may be broken down into organic substances by living organisms, for example, microorganisms.

For the purposes of the present invention, the term "amorphous" refers to a solid which is not crystalline, *i.e.*, has no lattice structure which is characteristic of a crystalline state.

For the purposes of the present invention, the term "crystalline" refers to a solid which has a lattice structure which is characteristic of a crystalline state.

For the purposes of the present invention, the term "high temperature deformation-resistant material" refers to a material which resists deformation at a temperature of about 140°F (60°C) or higher, for example, about 150°F (65.6°C) or higher.

For the purposes of the present invention, the term "high temperature deformable material" refers to a material which deforms at a temperature of less than about 140°F (60°C), for example, less than about 130°F (54.4°C).

For the purposes of the present invention, the term "thermoforming" refers to a method for preparing a shaped, formed, *etc.*, article from a thermoplastic sheet, film, *etc.* In thermoforming, the sheet, film, *etc.*, may be heated to its melting or softening point, stretched



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over or into a temperature-controlled, single-surface mold and then held against the mold surface until cooled (solidified). The formed article may then be trimmed from the thermoformed sheet. The trimmed material may be reground, mixed with virgin plastic, and reprocessed into usable sheet. Thermoforming may include vacuum forming, pressure forming, twin-sheet forming, drape forming, free blowing, simple sheet bending, *etc.*

For the purposes of the present invention, the term "thermoform" and similar terms such as, for example "thermoformed," *etc.*, refers to articles made by a thermoforming method.

For the purposes of the present invention, the term "melting point" refers to the temperature range at which a crystalline material changes state from a solid to a liquid, *e.g.*, may be molten. While the melting point of material may be a specific temperature, it often refers to the melting of a crystalline material over a temperature range of, for example, a few degrees or less. At the melting point, the solid and liquid phase of the material often exist in equilibrium.

For the purposes of the present invention, the term "$T_m$" refers to the melting temperature of a material, for example, a polymer. The melting temperature is often a temperature range at which the material changes from a solid state to a liquid state. The melting temperature may be determined by using a differential scanning calorimeter (DSC) which determines the melting point by measuring the energy input needed to increase the temperature of a sample at a constant rate of temperature change, and wherein the point of maximum energy input determines the melting point of the material being evaluated.

For the purposes of the present invention, the term "softening point" refers to a temperature or range of temperatures at which a material is or becomes shapeable, moldable, formable, deformable, bendable, extrudable, *etc.* The term softening point may include, but does not necessarily include, the term melting point.

For the purposes of the present invention, the term "$T_s$" refers to the Vicat softening point (also known as the Vicat Hardness). The Vicat softening point is measured as the temperature at which a polymer specimen is penetrated to a depth of 1 mm by a flat-ended needle with a 1 sq. mm circular or square cross-section. A load of 9.81 N is used. Standards for measuring Vicat softening points for thermoplastic resins may include JIS K7206, ASTM D1525 or ISO306,



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which are incorporated by reference herein.

For the purposes of the present invention, the term "$T_g$" refers to the glass transition temperature. The glass transition temperature is the temperature: (a) below which the physical properties of amorphous materials vary in a manner similar to those of a solid phase (*i.e.*, a glassy state); and (b) above which amorphous materials behave like liquids (*i.e.*, a rubbery state).

For the purposes of the present invention, the term "heat deflection temperature (HDT)" or heat distortion temperature (HDTUL) (collectively referred to hereafter as the "heat distortion index (HDI)") is the temperature at which a polymer deforms under a specified load. HDI is a measure of the resistance of the polymer to deformation by heat and is the temperature (in °C.) at which deformation of a test sample of the polymer of predetermined size and shape occurs when subjected to a flexural load of a stated amount. HDI may be determined by following the test procedure outlined in ASTM D648, which is herein incorporated by reference. ASTM D648 is a test method which determines the temperature at which an arbitrary deformation occurs when test samples are subjected to a particular set of testing conditions. This test provides a measure of the temperature stability of a material, *i.e.*, the temperature below which the material does not readily deform under a standard load condition. The test sample is loaded in three-point bending device in the edgewise direction. The outer fiber stress used for testing is 1.82 MPa, and the temperature is increased at 2°C/min until the test sample deflects 0.25 mm.

For the purposes of the present invention, the term "melt flow index (MFI)" (also known as the "melt flow rate (MFR)) refers to a measure of the ease of flow of the melt of a thermoplastic polymer, and may be used to determine the ability to process the polymer in thermoforming. MFI may be defined as the weight of polymer (in grams) flowing in 10 minutes through a capillary having a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. Standards for measuring MFI include ASTM D1238 and ISO 1133, which are herein incorporated by reference. The testing temperature used is 190°C with a loading weight of 2.16 kg. For thermoforming according to embodiments of the present invention, the MFI of the polymers may be in the range from 0 to about 20 grams per 10 minutes, for example from 0 to about 15 grams per 10 minutes.



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For the purposes of the present invention, the terms "viscoelasticity" and "elastic viscosity" refer interchangeably to a property of materials which exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials resist shear flow and strain linearly with time when a stress is applied, while elastic materials strain instantaneously when stretched and just as quickly return to their original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, exhibit time dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscoelasticity is the result of the diffusion of atoms or molecules inside of an amorphous material.

For the purposes of the present invention, the term "hydroxy aliphatic acids" refers to organic aliphatic carboxylic acids having a hydroxy group, and which may be used to provide polyhydroxyalkanoates. Hydroxy aliphatic acids useful herein may include lactic acid, hydroxy-beta-butyric acid (also known as hydroxy-3-butyric acid), hydroxy-alpha-butyric acid (also known as hydroxy-2-butyric acid), 3-hydroxypropionic acid, 3-hydroxyvaleric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, 3-hydroxyhexanoic acid, 4-hydroxyhexanoic acid, 6-hydroxyhexanoic acid, hydroxyacetic acid (also known as glycolic acid), lactic acid (also know as hydroxy-alpha-propionic acid), malic acid (also known as hydroxysuccinic acid), *etc.*, and mixtures thereof.

For the purposes of the present invention, the term "polyhydroxyalkanoate (PHA) polymer" refers broadly to renewable, thermoplastic aliphatic polyesters which may be produced by polymerization of the respective monomer hydroxy aliphatic acids (including dimers of the hydroxy aliphatic acids), by bacterial fermentation of starch, sugars, lipids, *etc.* PHA polymers may include poly-beta-hydroxybutyrate (PHB) (also known as poly-3-hydroxybutyrate), poly-alpha-hydroxybutyrate (also known as poly-2-hydroxybutyrate), poly-3-hydroxypropionate, poly-3-hydroxyvalerate, poly-4-hydroxybutyrate, poly-4-hydroxyvalerate, poly-5-hydroxyvalerate, poly-3-hydroxyhexanoate, poly-4-hydroxyhexanoate, poly-6-hydroxyhexanoate, polyhydroxybutyrate-valerate (PHBV), polyglycolic acid, polylactic acid (PLA), *etc.*, as well as PHA copolymers, blends, mixtures, combinations, *etc.*, of different PHA polymers, *etc.* PHA may be synthesized by methods disclosed in, for example, U.S. Pat. No. 7,267,794 (Kozaki *et al.*), issued September 11, 2007; U.S. Pat. No. 7,276,361 (Doi *et al.*),



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issued October 2, 2007; U.S. Pat. No. 7,208,535 (Asrar *et al.*), issued April 24, 2007; U.S. Pat. No. 7,176,349 (Dhugga *et al.*), issued February 13, 2007; and U.S. Pat. No. 7,025,908 (Williams *et al.*), issued April 11, 2006, the entire disclosure and contents of the foregoing documents being herein incorporated by reference.

For the purposes of the present invention, the term "polylactic acid or polylactide (PLA)" refers to a renewable, biodegradable, thermoplastic, aliphatic polyester formed from a lactic acid or a source of lactic acid, for example, renewable resources such as corn starch, sugarcane, *etc.* The term PLA may refer to all stereoisomeric forms of PLA including L- or D-lactides, and racemic mixtures comprising L- and D-lactides. For example, PLA may include D-polylactic acid, L-polylactic acid (also known as PLLA), D,L-polylactic acid, meso-polylactic acid, as well as any combination of D-polylactic acid, L-polylactic acid, D,L-polylactic acid and meso-polylactic acid. PLAs useful herein may have, for example, a number average molecular weight in the range of from about 15,000 and about 300,000. In preparing PLA, bacterial fermentation may be used to produce lactic acid, which may be oligomerized and then catalytically dimerized to provide the monomer for ring-opening polymerization. PLA may be prepared in a high molecular weight form through ring-opening polymerization of the monomer using, for example, a stannous octanoate catalyst, tin (II) chloride, *etc.*

For the purposes of the present invention, the term "starch-based polymer" refers to a polymer, or combination of polymers, which may be derived from, prepared from, *etc.*, starch. Starch-based polymers which may be used in embodiments of the present invention may include, for example, polylactic acid (PLA), thermoplastic starch (for example, by mixing and heating native or modified starch in the presence of an appropriate high boiling plasticizer, such as glycerin and sorbitol, in a manner such that the starch has little or no crystallinity, a low $T_g$, and very low water, *e.g.*, less than about 5% by weight, for example, less than about 1% water), plant starch (*e.g.*, cornstarch), *etc.*, or combinations thereof. See, for example, starch-based polymers, such as plant starch, disclosed in published PCT Pat App. No. 2003/051981 (Wang *et al.*), published June 26, 2003, the entire disclosure and contents of which are hereby incorporated by reference, *etc.*



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For the purposes of the present invention, the term "cellulose-based polymer" refers to a polymer, or combination of polymers, which may be derived from, prepared from, *etc.*, cellulose. Cellulose-based polymers which may be used in embodiments of the present invention may include, for example, cellulose esters, such as cellulose formate, cellulose acetate, cellulose diacetate, cellulose propionate, cellulose butyrate, cellulose valerate, mixed cellulose esters, *etc.*, and mixtures thereof.

For the purposes of the present invention, the term "mineral filler" refers to inorganic materials, often in particulate form, which may lower cost (per weight) of the polymer, and which, at lower temperatures, may be used to increase the stiffness and decrease the elongation to break of the polymer, and which, at higher temperatures, may be used to increase the viscosity of the polymer melt. Mineral fillers which may used in embodiments of the present invention may include, for example, talc, calcium chloride, titanium dioxide, clay, synthetic clay, gypsum, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium aluminate, magnesium carbonate mica, silica, alumina, sand, gravel, sandstone, limestone, crushed rock, bauxite, granite, limestone, glass beads, aerogels, xerogels, fly ash, fumed silica, fused silica, tabular alumina, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, ceramic materials, pozzolanic materials, zirconium compounds, xonotlite (a crystalline calcium silicate gel), lightweight expanded clays, perlite, vermiculite, hydrated or unhydrated hydraulic cement particles, pumice, zeolites, exfoliated rock, *etc.*, and mixtures thereof

For the purposes of the present invention, the term "molded" refers to any method for casting, shaping, forming, extruding, *etc.*, softened or melted polymers, layers, composites, *etc.*, of the present invention.

For the purposes of the present invention, the term "blow molded" refers to a method of molding in which the material is melted and extruded into a hollow tube (also referred to as a parison). This parison may then be captured by closing it into a cooled mold and air is then blown into the parison, thus inflating parison into the shaped article. After the shaped article has cooled sufficiently, the mold is opened and the article is released (*e.g.*, ejected).



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For the purposes of the present invention, the term "compression molded" refers to a method of molding in which the molding material, with optional preheating, is first placed in an open, heated mold cavity. The mold is closed with a top force or plug member, pressure is applied to force the material into contact with all mold areas, and heat and pressure are maintained until the molding material has cured.

For the purposes of the present invention, the term "core" refers to that portion of the thermoformable composite which comprises a renewable polymer (or polymers) having an HDI value of up to about 90°C, for example, up to about 60°C (*e.g.*, up to about 54°C). In other words, the core comprises renewable polymers which are not resistant to deformation at temperatures of about 90°C or greater, and may not be resistant to deformation at lower temperatures, for example, about 60°C or lower (*e.g.*, about 54°C or lower).

For the purposes of the present invention, the term "heat-resistant layer" refers to a layer of the thermoformable composite which comprises a heat-resistant polymer (or polymers) for imparting heat resistance to the thermoformable composite.

For the purposes of the present invention, the term "heat-resistant polymer" refers to a polymer (or polymers) which has an HDI value of greater than about 50°C, for example greater than about 65°C (*e.g.*, greater than about 90°C). In other words, heat-resistant polymers are resistant to deformation at temperatures above about 50°C, for example, above about 65°C (*e.g.*, above about 90°C). Heat-resistant polymers may or may not renewable polymers and may include polyolefins (*e.g.*, polyethylene, polypropylene, *etc.*), polystyrenes, polyesters, polyamides, polyimides, polyurethanes, cellulose-based polymers, such as cellulose propionate, *etc.*, and combinations thereof.

For the purposes of the present invention, the term "CAP layer" (also sometimes known as a "skin" layer) refers to an outer layer which substantially surrounds the core.

For the purposes of the present invention, the term "tie layer" refers to an adhesive layer (*e.g.*, a self-adhesive layer, a thermally meltable adhesive layer, *etc.*) between two other layers that attaches, adheres, glues, fuses, bonds, *etc.*, these other layers to one another. Tie layers may be used to attach, adhere, glue, fuse, bond, *etc.*, two layers together that are otherwise difficult



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to adhere together or cannot be adhered to another because of differing compositions, differing coefficients of thermal expansion, differing coefficients of friction or adhesion, *etc.* For example, a tie layer may be used to attach, adhere, glue, fuse, bond, *etc.*, the outer heat-resistant layer to the core. Suitable tie layers may be comprised of one or more adhesive materials, one or more film-forming thermoplastic polymeric materials, or combinations of adhesive and film-forming thermoplastic polymeric materials. These adhesive materials may include ethyl vinyl acetate (EVA), copolymerized ethylene and methacrylic or acrylic acid, such as Nucrel®, ionomers polymers such as Surlyn®, low density polyethylene (LDPE) treated with maleic anhydride, *etc.*, as well as combinations thereof.

For the purposes of the present invention, the term "substantially surrounds" refers to heat-resistant layer which surrounds at least about 90% of the surface of the core, for example, at least about 95% of the surface of the core. For example, substantially surrounds may include leaving only the ends of core exposed when; for example, the core is positioned between two heat-resistant layers.

For the purposes of the present invention, the term "sheet" refers to webs, strips, films, pages, pieces, segments, *etc.*, which may be continuous in form (*e.g.*, webs) for subsequent subdividing into discrete units, or which may be in the form of discrete units (*e.g.*, pieces).

For the purposes of the present invention, the term "extrusion" refers to a method for shaping, molding, forming, *etc.*, a material by forcing, pressing, pushing, *etc.*, the material through a shaping, forming, *etc.*, device having an orifice, slit, *etc.*, for example, a die, *etc.* Extrusion may be continuous (producing indefinitely long material) or semi-continuous (producing many short pieces, segments, *etc.*).

For the purposes of the present invention, the term "coextrusion" and similar terms, such as, for example, "coextruded," refers to refers to the extrusion of multiple layers of material (*e.g.*, polymers) simultaneously. Coextrusion may utilize two or more extruders to melt and deliver a steady volumetric throughput of different molten materials to a single extrusion head which may combine the materials in the desired extruded shape.



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For the purposes of the present invention, the term "interpenetrating network" refers to where two adjacent areas, domains, regions, layers, *etc.*, merge, combine, unite, fuse, *etc.*, together so that there is essentially no boundary therebetween.

For the purposes of the present invention, the term "thermoplastic" refers to the conventional meaning of thermoplastic, *i.e.*, a composition, compound, material, *etc.*, that exhibits the property of a material, such as a high polymer, that softens when exposed to sufficient heat and generally returns to its original condition when cooled to room temperature. Thermoplastics may include, but are not limited to, polyesters (*e.g.*, polyhydroxyalkanoates, polyethyleneterephthalate, *etc.*), poly(vinylchloride), poly(vinyl acetate), polycarbonates, polymethylmethacrylate, cellulose esters, poly(styrene), poly(ethylene), poly(propylene), cyclic olefin polymers, poly(ethylene oxide), nylons, polyurethanes, protein polymers, *etc.*

For the purposes of the present invention, the term "plasticizer" refers to the conventional meaning of this term as an agent which softens a polymer, thus providing flexibility, durability, *etc.* Plasticizers may be advantageously used in amounts of, for example, from about 0.01 to about 45% by weight, *e.g.*, from about 3 to about 15% by weight of the polymer, although other concentrations may be used to provide desired flexibility, durability, *etc.* Plasticizers which may used in embodiments of the present invention include, for example, aliphatic carboxylic acids, aliphatic carboxylic acid metal salts, aliphatic esters, aliphatic amides, alkyl phosphate esters, dialkylether diesters, dialkylether esters, tricarboxylic esters, epoxidized oils and esters, polyesters, polyglycol diesters, alkyl alkylether diesters, aliphatic diesters, alkylether monoesters, citrate ester, dicarboxylic esters, vegetable oils and their derivatives, esters of glycerine, ethers, *etc.*, and mixtures thereof. For example, with starch-based polymers (*e.g.*, plant starch), the plasticizers may include one or more aliphatic acids (*e.g.*, oleic acid, linoleic acid, stearic acid, palmitic acid, adipic acid, lauric acid, myristic acid, linolenic acid, succinic acid, malic acid, cerotic acid, *etc.*), one or more low molecular weight aliphatic polyesters, one or more aliphatic amides (*e.g.*, oleamide, stearamide, linoleamide, cycle-n-lactam, ε-caprolactam, lauryl lactam, N,N-dibutyl stearamide, N,N-dimethyl oleamide, *etc.*), one or more aliphatic carboxylic acid esters (*e.g.*, methoxyethyl oleate, diisooctyl sebacate, bis(2-butoxyethyl) adipate, dibenzyl sebacate, isooctyl- isodecyl adipate, butyl epoxy fatty acid ester, epoxidized butyl



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acetoricinoleate, and low molecule weight (300-1200) poly(1,2-propylene glycol adipate, *etc.*), one or more aliphatic carboxylic acid metal salts (*e.g.*, magnesium oleate, ferrous oleate, magnesium stearate, ferrous stearate, calcium stearate, zinc stearate, magnesium stearate, zinc stearate pyrrolidone, *etc.*) See published PCT Pat App. No. 2003/051981 (Wang *et al.*), published June 26, 2003, the entire disclosure and contents of which are hereby incorporated by reference.

For the purposes of the present invention, the term "compatibilizer" refers to a composition, compound, *etc.*, used to enhance reextrusion of polymer(s), plastic trim, *etc.*, in thermoforming recycle operations by causing what may be two or more dissimilar polymers to provide a homogeneous, or more homogeneous, melt during reextrusion, and to avoid or minimize disassociation when recycled material is added back to the polymer feedstock being extruded. Compatibilizers which may be used in embodiments of the present invention include, for example, polyolefins, polybutadienes, polystyrenes, *etc.*, modified with maleic anhydride, citrates of fatty acids, glycerol esters, *etc.* The compatibilizer may be advantageously used in amounts from about 0.005 to about 10% by weight, for example from about 0.01 to about 5% by weight of the polymer, although other concentrations may be used so long as they are effective at keeping the two or more polymers miscible and more homogeneous. Maleated polyolefins/polybutadienes/polystyrenes are commercially available compatibilizers, sold by Eastman (EPOLENES®), Crompton (POLYBONDS®), Honeywell (A-C®), and Sartomer (Ricons®). Maleated and epoxidized rubbers, derived from natural rubbers, may also be useful as compatibilizers, for example, maleic anhydride grafted rubber, epoxy/hydroxyl functionalized polybutadiene, *etc.* Other carboxylic acid modified polyolefin copolymers, such as those from succinic anhydride, may also be used. Monomers such as maleic anhydride, succinic anhydride, *etc.*, may also be added directly along with or without other commercial compatibilizers to prepare in situ compatabilized blends. See U.S. Pat. No. 7,256,223 (Mohanty *et al.*), issued August 14, 2007, the entire disclosure and contents of which is hereby incorporated by reference. Other useful compatibilizers may include poly(2-alkyl-2-oxazolines), such as, for example, poly(2-ethyl-2-oxazoline) (PEOX), poly(2-propionyl-2-oxazoline), poly(2-phenyl-2-oxazolone), *etc.* See U.S. Pat. No. 6,632,923 (Zhang *et al.*), issued October 14, 2003, the entire disclosure and contents of which is hereby incorporated by reference. These compatibilizers may be



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included singly or as combinations of compatibilizers. For example, with starch-based polymers (*e.g.*, plant starch), the compatibilizers may include one or more products (or complexes) of co-monomers and anhydrides (or their derivatives) at, for example, a 1:1 mole ratio), wherein the co-monomer may include one or more of: acrylonitrile, vinyl acetate, acrylamide, acrylic acid, glutaric acid, methacrylate, styrene, *etc.*, and wherein the anhydride (or derivative) may include one or more of: acetic anhydride, methacrylic acid anhydride, succinic anhydride, maleic anhydride, maleimide, *etc.* See published PCT Pat App. No. 2003/051981 (Wang *et al.*), published June 26, 2003, the entire disclosure and contents of which are hereby incorporated by reference.

For the purposes of the present invention, the term "significant weight amount" refers to an amount of the renewable polymer which may be at least about 50% by weight of the composite, for example, at least about 80% by weight, (*e.g.*, at least about 90% by weight) of the composite.

***Description***

Much work has been done on modifying PLA to survive storage and distribution conditions involving higher temperatures (*e.g.*, above about 140°F (60°C)) that may cause deformation of articles comprising PLA due to gravity, residual mold stress, *etc.* Modification methods have included the addition of mineral fillers (talc, calcium carbonate, or nanoclay) to PLA or small amounts of fossil fuel resins and adjuvants. These methods may improve the performance of the PLA-containing articles in heat distortion test apparatus, but may also do little to improve the performance of these articles during higher temperature storage or transportation. The use of additives with the PLA may be ineffective where the overall blend has PLA as a continuous phase. The mechanical strength of the PLA articles under slow temperature changes and small strain rates may be dominated by the strength of the continuous phase. While heat distortion temperature may be a widely used analysis method throughout the plastics industry, it has different mechanical conditions which may not be relevant to the storage condition issue.



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In embodiments of the present invention, articles comprising a thermoformable composite are provided which comprise: a core and a heat-resistant outer layer substantially surrounding the core. The core comprises a renewable polymer and/or natural fiber having: (a) a $T_s$ value of up to about 90°C (*e.g.*, in the range of from about 40° to about 90°C); (b) a heat distortion index of up to about 90°C (*e.g.*, up to about 60°C, for example, up to about 54°C); and (c) optionally, a $T_m$ in the range of from about 40° to about 250°C (*e.g.*, in the range of from about 90° to about 190°C). The outer heat-resistant layer comprises a heat-resistant polymer having: (a) a $T_s$ value of greater than about 60°C (*e.g.*, greater than about 75°C, for example, greater than about 100°C); (b) a heat distortion index of greater than about 50°C (*e.g.*, greater than about 65°C, for example, greater than about 90°C); and (c) optionally, a $T_m$ greater than about 60°C (*e.g.*, greater than about 100°C, for example, greater than about 150°C; (b). The $T_s$ value, heat distortion index (and optionally $T_m$) of the heat-resistant polymer is also greater than that of the renewable polymer, for example, the heat-resistant polymer has a $T_s$ value, heat distortion index (and optionally $T_m$) at least about 5°C greater (*e.g.*, at least about 10°C greater) than that of the renewable polymer. The renewable polymer comprises at least about 60% by weight (*e.g.*, at least about 80% by weight, for example, at least about 90% by weight) of the composite. Such articles provide the ability to resist deformation during higher temperature conditions that may occur during storage and distribution.

Embodiments of the present invention may include the use of laminar or laminated composite structures wherein the core comprises renewable PHAs, such of PLA, and wherein the outer layer comprises heat-resistant polymers such as polystyrene, polypropylene, *etc.*, to make a high temperature deformation-resistant thermoformed article. One embodiment may comprise a laminate composite structure formed with an upper (first) layer of a heat-resistant polymer, a middle (core) of PLA, and a bottom or lower (second) layer of a heat-resistant polymer. The overall PLA content of the composite structure may be very high, *e.g.*, at least about 80 % by weight of the composite structure. For example, 90% PLA content may be obtained by making a thermoformable structure which comprises 1 mil thick upper (first) layer of heat-resistant polymer, 20 mil thick middle (core) of PLA, and 1 mil thick bottom or lower (second) layer of heat-resistant polymer. At temperatures above those encountered in transportation such as, for example, about 150°F (65.6°C) or higher, the heat-resistant polymer-containing layers would



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provide enough strength for the article to resist distribution and storage stresses, even though the PLA core may have lost its mechanical strength. When the higher temperature condition is removed, the PLA may regain its original strength without deformation.

In one embodiment of the present invention, the core may comprise a combination of renewable starch-based polymers with other materials, *e.g.*, one or more plasticizers, one or more compatibilizers, one or more other polymers, *etc.* For example, the core may comprise from about 20% to about 95% by weight of a combination comprising at least about 60% by weight (*e.g.*, from about 65 to about 95% by weight) plant starch, and up to about 40% other materials, for example, from about 1 to about 15% by weight plasticizer (such as those previously described for starch-based polymers), from about 0.1 to about 5% by weight compatibilizer (such as those previously described for starch-based polymers), and from about 1 to about 20% by weight biodegradable polymer other than plant starch (such as polylactic acid and polyhydroxybutyrate-valerate). Useful combinations of this type may include Plastarch Materials (PSM), such as HL-102 series granular material, made by Wu Han Hua Li Environment Protection Science & Technology Co., Ltd., of Wu Han Optic Valley, China), and which are disclosed in published PCT Pat App. No. 2003/051981 (Wang *et al.*), published June 26, 2003, the entire disclosure and contents of which are hereby incorporated by reference.

One embodiment of the present invention may be a thermoformed article such as a food or beverage cup, lid, cutlery item, foodservice item, molded tray, food storage container, *etc.* Another embodiment of the present invention may be an article in the form of a thermoformed sheet comprising a core of renewable polymer between two layers comprising a heat-resistant polymer. Another embodiment of the present invention may be an article wherein the core comprising a renewable polymer may be blended with other non-renewable polymers. Another embodiment of the present invention may be an article wherein the core comprises a renewable polyhydroxyalkanoate polymer which may contain chain branching moieties or wherein the core comprises other additives, such as plasticizers, compatibilizers, *etc.*, to change the properties of the core. Another embodiment of the present invention may be an article wherein the one or more of the core or outer layers may comprise one or more mineral fillers, for example, talc, calcium chloride, titanium dioxide, clay, *etc.*, or mixtures thereof.



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In embodiments of the present invention, a thermoformable composite may be provided by coextruding a heat-resistant polymer having the above defined $T_s$, heat distortion index, and optional $T_m$ values, and renewable polymer having the above defined $T_s$, heat distortion index and optional $T_m$ values, wherein the renewable polymer in the core comprises a significant weight amount of the composite (for example, at least about 80% by weight), and wherein the heat-resistant polymer forms an outer layer which substantially surrounds the core (for example, at least about 90% of the surface area of the core, such as at least about 95% of the surface area of the core). Articles such as, for example, a food or beverage cup, lid, cutlery item, foodservice item, molded tray, food storage container, *etc.*, may then thermoformed from the composite structure.

Another embodiment of the present invention may be an article wherein the core or one or more outer layers may comprise a compatibilizer which enhances reextrusion of polymer or plastic trim pieces obtained during trimming of the article which may be used in thermoforming recycle operations. Another embodiment of the present invention may be an article formed by compression molding or blow molding the thermoformable composite. Another embodiment of the present invention may be an article formed from a coextruded sheet from a roll fed through thermoforming operation, for example, with inline extrusion and thermoforming with recycle of trimmed polymer or plastic for regrinding.

Referring to the drawings, an embodiment an article comprising a thermoformable laminate composite according to the present invention is illustrated in FIG. 1 in the form of, for example, a beverage lid, indicated as 100. Beverage lid 100 comprises an outer rim portion, indicated as 104, a center portion, indicated as 108, and a main body portion, indicated as 112, connecting center portion 108 and rim portion 104.

FIG. 2 is a sectional view of the beverage lid 100 to illustrate the composition of the various layers and core comprising a thermoformable laminate composite. As shown in FIG. 2, the thermoformable laminate composite comprises a thicker core 204 comprising a renewable polymer, for example, a polyhydroxyalkanoate polymer, such as polylactic acid (PLA), a starch-based polymer, a cellulose-based polymer, *etc.*, plus any other optional components such as plasticizers, compatibilizers, *etc.* Core 204 is positioned between a first upper heat-resistant



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layer 208 comprising a heat-resistant polymer, such as polystyrene, polypropylene, cellulose propionate, *etc.*, and a second lower or bottom heat-resistant layer 212 which also comprises a heat-resistant polymer which may be the same or different from the heat-resistant polymer in first layer 204. The upper interface, indicated as 216, between first layer 208 and core 204, may be a distinct interface between layer 208 and core 204, or may comprise an interpenetrating network of layer 208 and core 204, may include a tie layer between layer 208 and core 204, *etc.* Similarly, the lower interface, indicated as 220, between second layer 212 and core 204, may be a distinct interface between layer 212 and core 204, or may comprise an interpenetrating network of layer 212 and core 204, may include a tie layer between layer 212 and core 204, *etc.*

An embodiment of the method of the present invention for preparing a thermoformed article is further schematically illustrated in FIG. 3 which shows thermoforming system, indicated generally as 300. In system 300, pellets of a renewable polymer such as PLA, are added, as indicated by arrow 304, to a core extruder, indicated as 308. Similarly, pellets of a heat resistant polymer, such as polystyrene, polypropylene, *etc.*, are added, as indicated by arrow 312, to an outer (CAP) layer extruder, indicated as 316. Core extruder 308 provides an extruded core, indicated by arrow 320, while CAP layer extruder 312 provides an extruded CAP layer, indicated by arrow 324. Core 320 and CAP layer 324 are combined in a coextruder, indicated as 328, and may be coextruded at a temperature in the range of, for example, from about 155° to about 300°C (*e.g.*, from about 200° to about 225°C). In coextruder 328, CAP layer 324 surrounds core 320 to provide a hot coextruded laminate, indicated as 332.

Hot laminate 332 passes through a series chill rolls, indicated generally as 336, to lower to the temperature of the laminate to provide cold web laminate composite, indicated as 340 to, for example, in the range of from about 25° to about 150°C (*e.g.*, from about 60° to about 75°C). Cold laminate composite web 340 passes through a remelt oven, indicated as generally 344, where cold laminate composite web 340 is softened or melted at a temperature, for example, in the range of from about 100° to about 200°C (*e.g.*, from about 120° to about 180°C)., to provide a thermoformable laminate composite web, indicated generally as 348. Thermoformable laminate composite web 348 is passed through a thermoforming or molding section at a temperature , for example, in the range of from about 25° to about 75°C (*e.g.*, from about 26° to about 40°C), indicated generally as 352, to provide a thermoformed or molded articles, of three are



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schematically shown and indicated as 356-1, 356-2 and 356-3. Thermoformed article 356-2 is shown as passing through a trimmer press 358 for remove excess material (*e.g.*, flashing) to provide finished article 356-3, which may then exits system 300, as indicated by arrow 360.

The trimmed material from article 356-2 many be recycled, as indicated by arrow 364. Recycled material 364 is sent to a chopper or grinder, indicated as 368, to provide size reduced recycled material. The size reduced recycled material is then returned, as indicated by arrow 372 for blending with PLA pellets in core extruder 308.

Fig. 4 is a graph which shows a typical Differential Scanning Calorimetry (DSC) Spectrum of PLA. It illustrates a Glass transition temperature ($T_g$) around 60°C, a Crystallization Temperature ($T_c$) at 107°C, and a Melting Temperature ($T_m$) at 145°C.

Fig. 5 is a graph which shows a differential Scanning Calorimetry (DSC) Spectra of PLHB120 and PLHE24. It illustrates a big decrease of Glass transition temperature ($T_g$) from around 60°C to 14 and 24°C, and similar Melting Temperature ($T_m$) at 145°C comparing to the data in Figure 1. These data suggested the thermal property modification of the samples.

Fig. 6 is a graph which shows a differential Scanning Calorimetry (DSC) Spectra of PLHL34 and PLHL89. It illustrates a decrease of Glass transition temperature ($T_g$) from around 60°C to 47and 50°C, obviously change of Crystallization Temperature ($T_c$), and much higher Melting Temperature ($T_m$) at 171°C comparing to the data in Figure 1. These data suggested the thermal property modification of the samples.

It should be appreciated that the embodiments illustrated in FIGS. 1 to 6 are provided to illustrate the teachings of the present invention. Alterations or modifications within the skill of the art of the embodiments in FIGS. 1 to 3 are considered within the scope of the present invention, so long as these alterations or modifications operate in a same or similar manner, function, *etc.*



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## EXAMPLES

General formulations of core polymers are shown in the following Tables 1 and 2:

Table 1

| General Formulation No. | PSM[1] | PP[2] | Tenite[3] | PLA/MPLA[4] |
|---|---|---|---|---|
| 1 | 90-95% | 5-10% | 0% | 0% |
| 2 | 90-95% | 0% | 5-10% | 0% |
| 3 | 80-90% | 5-10% | 5-10% | 0% |
| 4[5] | 20-52% | 0% | 23-37% | 24-50% |

[1]Plastarch Materials: starch-based resin comprising plant starch, plasticizer, compatibilizer and biodegradable polymer made by Wu Han Hua Li Environment Protection Science & Technology Co., Ltd., of Wu Han Optic Valley, China. PSM comprises 100% biodegradable materials and greater than about 95% biobased (renewable) materials. PSM may be processed at temperatures in the range of, for example, from about 155° to about 210°C.

[2]Polypropylene (extrusion grade)

[3]Cellulose propionate (from Eastman Chemicals)

[4]PLA: polylactic acid; MPLA: maleic anhydride modified PLA, which is used as a compatibilizer for blends of PLA and PSM. Ratio PLA:MPLA may be in range of from about 100:0.2 to about 1:2.

[5]Total renewable polymer in the range of from about 60 to about 88% by weight.

The general formulations shown in Table 1 are prepared by feeding mixtures of resin pellets for each listed polymer (within the percentages indicated) into a single or twin extruder and extruded at temperatures in the range of, for example, from about 155° to about 210°C. Outer skin layers (*i.e.*, upper and lower CAP layers) are also prepared by coextrusion of polystyrene (Chevron MC3100), polypropylene and/or Tenite with the core. Cores prepared from general formulations nos. 1-4 may have thicknesses of in the range of from about 12 to



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about 18 mils. For general formulation no. 1, skin layers of polypropylene may be prepared having thicknesses of in the range of from about 1 to about 5 mils. For general formulation no. 2, skin layers of polypropylene or Tenite may be prepared having thicknesses of in the range of from about 1 to about 5 mils. For general formulation no. 3, skin layers of polypropylene may be prepared having thicknesses of in the range of from about 1 to about 5 mils. For general formulation no. 4, skin layers of polystyrene, polypropylene or Tenite are prepared having thicknesses of in the range of from about 1 to about 5 mils.

Table 2 Blending of PLA and PHA with / Without additives

| | PLA Resin, % | | | | Additives | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Run # | A | B | C | PHA | E243 | E283 | E285 | Temperature, C | Speed | Torq. |
| 1 | 100.0 | | | | | | | 170 | low | 7.0 |
| 2 | | 100.0 | | | | | | 170 | low | 8.5 |
| 3 | | | 100.0 | | | | | 170 | low | 10.0 |
| 4 | | | 90.0 | 10.0 | | | | 170 | low | 8.5 |
| 5 | | | 85.0 | 10.0 | 5.0 | | | 170 | low | 8.5 |
| 6 | | | 80.0 | 20.0 | | | | 170 | low | 7.5 |
| 7 | | | 80.0 | 15.0 | 5.0 | | | 170 | low | 8.0 |
| 8 | | | 80.0 | 15.0 | | 5.0 | | 170 | low | 7.0 |
| 9 | 100.0 | | | | | | | 180 | low | 6.0 |
| 10 | | | 80.0 | 15.0 | 5.0 | | | 180 | low | 5.2 |
| 11 | | | 85.0 | 10.0 | 5.0 | | | 180 | low | 6.2 |
| 12 | | | 80.0 | 15.0 | | | 5.0 | 180 | low | 5.4 |
| 13 | 100.0 | | | | | | | 190 | low | 4.6 |
| 14 | | | 80.0 | 15.0 | 5.0 | | | 190 | low | 4.0 |
| 15 | | | 90.0 | | 10.0 | | | 190 | low | 6.0 |
| 16 | | 100.0 | | | | | | 190 | low | 5.5 |
| 17 | | | 80.0 | 15.0 | 5.0 | | | 180 | high | 5.8 |
| 18 | | | 90.0 | | 10.0 | | | 180 | high | 8.5 |
| 19 | 100.0 | | | | | | | 180 | high | 5.3 |
| 20 | | | 80.0 | 15.0 | 5.0 | | | 180 | low | 5.3 |

Table 2 contains blend information and twin screw extruder (a Haake PolyDrive Mixer, which is an extruder with two screws) processing conditions for the experimental blends tested. The PLA resin (2002D) is a product of Natural Works LLC. The PHA (1000P) is a product of Ningbo Tian'an Biological Materials Co., Ltd.



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**Table 3 BioResin Formulation and Their Heat Resistance**

| | Component | % | Extrusion Temp, F | 200 F test | Aging test |
|---|---|---|---|---|---|
| Formula | PLA | 52.0% | | | |
| PLHE24 | PHA | 38.0% | | | |
| | E243 | 10.0% | | | |
| | | | 380 | pass | pass |
| | | | | | |
| Formula | PLA | 52.0% | | | |
| PLHE28 | PHA | 38.0% | | | |
| | E283 | 10.0% | | | |
| | | | 350 | pass | pass |
| | | | | | |
| Formula | PLA | 52.0% | | | |
| PLHB120 | PHA | 38.0% | | | |
| | BS120 | 10.0% | | | |
| | | | 380 | pass | pass |
| | | | | | |
| Formula | PLA | 52.0% | | | |
| PLHL89 | PHA | 38.0% | | | |
| | LA89K | 10.0% | | | |
| | | | 350 | pass | pass |
| | | | | | |
| Formula | PLA | 52.0% | | | |
| PLHL34 | PHA | 38.0% | | | |
| | L3410 | 10.0% | | | |
| | | | 380 | fail | pass |
| | | | | | |
| Formula | PSM102 | 80.0% | | | |
| PSP80 | PP | 20.0% | | | |
| | | | 380 | pass | pass |

Table 3 contains blend information, twin screw extruder (a Brabender PS/6, which is an extruder with two screws) processing conditions, and testing results of the experimental blends. 200 F testing is to place the specimen into a 200°F oven for 30 minutes, and the PASS means there is no deformation of the sample, and the FAIL means there is. The Aging test is to place the specimen into a 150°F oven for 3 weeks, and the PASS means the sample doesn't turn brittle, and the FAIL means it does.



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| Table 4 PHA-PLA Pilot Plant Run Results | | | | | | | |
|---|---|---|---|---|---|---|---|
| Run # | PHA, % | PLA, % | BS120, % | L8900, % | E243, % | L3410, % | 200 F test |
| 1 | 38.00 | 52.00 | 10.00 | | | | pass |
| 2 | 38.00 | 52.00 | | 10.00 | | | pass |
| 3 | 38.00 | 52.00 | | | 10.00 | | pass |
| 4 | 38.00 | 52.00 | | | | 10.00 | pass |

Table 4 contains blend information on a single screw extruder (which is an extruder with one screw), and testing results of the experimental blends. The 200 F testing is the same as that in the Table 3.

Table 5 Formula with Modified PLA

| | PHA, % | PLA, % | BS120, % | E243, % | E285, % | E283, % | S3202, % | L1706, % |
|---|---|---|---|---|---|---|---|---|
| Run # | | | | | | | | |
| 1 | 45.00 | 45.00 | 10.00 | | | | | |
| 2 | 47.50 | 47.50 | 5.00 | | | | | |
| 3 | 63.00 | 27.00 | 10.00 | | | | | |
| 4 | 66.50 | 28.50 | 5.00 | | | | | |
| 5 | 45.00 | 45.00 | | 10.00 | | | | |
| 6 | 45.00 | 45.00 | | | 10.00 | | | |
| 7 | 45.00 | 45.00 | | | | 10.00 | | |
| 8 | 45.00 | 45.00 | | | | | 10.00 | |
| 9 | 45.00 | 45.00 | | | | | | 10.00 |
| 10 | 28.50 | 66.50 | | | | 5.00 | | |
| 11 | 28.50 | 66.50 | | | | | | 5.00 |
| | | | | | | | | |
| | MA-PLA*, % | PLA, % | Starch-Glycerol (64:36) | | Starch-Glycerol (73:27) | | | |
| 12 | 25.00 | 30.00 | 45.00 | | | | | |
| 13 | 25.00 | 30.00 | | | 45.00 | | | |
| 14 | 5.00 | 15.00 | 80.00 | | | | | |
| 15 | 12.00 | 38.00 | 50.00 | | | | | |
| 16 | 5.00 | 15.00 | | | 80.00 | | | |
| 17 | 12.00 | 38.00 | | | 50.00 | | | |
| | | | | | | | | |
| | *: MA-PLA: pla/ma/bpo = 97.5/2.0/0.5 | | | | Starch: Tate & Lyle Pearl Cron Starch | | | |

Table 5 contains blend information of PLA, PHA and various additives on a twin screw extruder (a Brabender PS/6, which is an extruder with two screws), where MA is maleic anhydride, bpo is benzoyl peroxide.



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| Table 6 Bio-Resin Blends with Natural Fiber | | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Run # | PLA, % | Tenite, % | PSM, % | Cellulose Fiber, % | Temperature, C |
| R6 - 1 | 70 | | | 30 | 205 |
| R6 - 2 | | 16 | 64 | 20 | 202 |
| R6 - 3 | | 32 | 48 | 20 | 198 |
| R6 - 4 | | 48 | 2 | 20 | 196 |
| R6 - 5 | 43 | 37 | | 20 | |
| R6 - 6 | 43 | 37 | | 20 | |

Table 6 contains blend information of Natural Fiber containing formulas and twin screw extruder ( a Brabender PS/6, which is an extruder with two screws) processing conditions for the experimental blends tested, where PSM is a starch based resin (HL-102) produced by Wuhan Huali Environment Protection Science & Technology Co., Ltd., Tenite is a Cellulose Propionates (Tenite 337E) of Eastman Chemical Co., while the Cellulose Fiber (TC-750) is a product of Creafill Fibers Corp.

All documents, patents, journal articles and other materials cited in the present application are hereby incorporated by reference.

Although the present invention has been fully described in conjunction with several embodiments thereof with reference to the accompanying drawings, it is to be understood that various changes and modifications may be apparent to those skilled in the art. Such changes and modifications are to be understood as included within the scope of the present invention as defined by the appended claims, unless they depart therefrom.



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**WHAT IS CLAIMED IS:**

1. An article comprising a thermoformable composite comprising:

a core comprising a renewable polymer and/or natural fiber having: (a) a $T_s$ value of up to about 90°C; and (b) a heat distortion index of up to about 90°C; and

a heat-resistant outer layer substantially surrounding the core and comprising a heat-resistant polymer having: (a) a $T_s$ value of greater than about 60°C; and (b) a heat distortion index of greater than about 50°C;

wherein the renewable polymer and/or natural fiber comprises at least about 50% by weight of the composite;

wherein the heat-resistant polymer has a $T_s$ value and heat distortion index greater than that of the renewable polymer and/or natural fiber.

2. The article of claim 1 wherein the renewable polymer and/or natural fiber comprises a polyhydroxyalkanoate polymer, a polycaprolactone polymer, a starch-based polymer, a cellulose-based polymer, or combination thereof.

3. The article of claim 2 wherein the natural fiber are cellulose fibers and powders, rice fiber husk fiber, wheat barn fiber, straw fiber, corn cob fiber, wood fibers, and bamboo fibers.

4. The article of claim 2 the renewable polymer comprises a polyhydroxyalkanoate polymer.

5. The article of claim 4, wherein the polyhydroxyalkanoate polymer comprises one or more of poly-beta-hydroxybutyrate, poly-alpha-hydroxybutyrate, poly-3-hydroxypropionate, poly-3-hydroxyvalerate, poly-4-hydroxybutyrate, poly-4-hydroxyvalerate, poly-5-hydroxyvalerate, poly-3-hydroxyhexanoate, poly-4-hydroxyhexanoate, poly-6-hydroxyhexanoate, polyhydroxybutyrate-valerate, polyglycolic acid, or polylactic acid.



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6. The article of claim 5, wherein wherein the polyhydroxyalkanoate polymer comprises polylactic acid.

7. The article of claim 5, wherein the polylactic acid has a number average molecular weight in the range of from about 15,000 and about 500,000.

8. The article of claim 1, wherein the outer layer comprises a first and a second layer, and wherein the core is positioned between the first and second layers.

9. The article of claim 8, wherein an interface is formed between the core and each of the first and second layers, and wherein one or more of the interfaces provides an interpenetrating network.

10. The article of claim 1, which is in the form of a food or beverage cup, lid, cutlery item, foodservice item, molded tray, or food storage container.

11. The article of claim 10, which is in the form of a beverage lid.

12. An article comprising a thermoformable composite comprising:
a single layer having a combination of renewable polymer and natural fillers contained therein wherein the single layer comprising at least about 50% by weight bio-based material.

13. The article of claim 12, wherein the bio-based material comprises cellulose fibers and powders, rice fiber husk fiber, wheat barn fiber, straw fiber, corn cob fiber, wood fibers, and bamboo fibers.

14. The article of claim 12, which is designed to be totally degraded in a natural environment or in a composter, preferably in a time period that is significantly shorter than that required for the degradation of conventional polymer or plastic materials.

15. The article of claim 12, which is selected from the group consisting of utensils, food serviceware, forks, spoon, knives, containers, bottles, foam material products, plates and pots or films, trash bags, grocery bags, drinking straws, spun-bonded non-woven material and sheets.



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16. A process for preparing a biodegradable polymer composition useful for manufacturing bio-based biodegradable articles, the process comprising:

(1) providing a renewable polymer and/or natural fiber having: (a) a $T_s$ value of up to about 90°C; and (b) a heat distortion index of up to about 90°C;

(2) providing a heat-resistant polymer having: (a) a $T_s$ of greater than about 60°C; and (b) a heat distortion index greater than about 50°C, wherein the $T_s$ value and heat distortion index of the heat-resistant polymer is greater than that of the renewable polymer and/or natural fiber; and

(3) coextruding the heat-resistant polymer and the renewable polymer to provide a thermoformable composite comprising:

a core comprising the renewable polymer and/or natural fiber, wherein the renewable polymer and/or natural fiber comprises at least about 50% by weight of the composite; and

a heat-resistant outer layer comprising the heat-resistant polymer which substantially surrounds the core.

17. The process of claim 16, which comprises the further step (4) of lowering the temperature of composite after step (3) to provide a cold composite web.

18. The process of claim 17, which comprises the further steps of:

(5) softening or melting the cold composite web to provide a thermoformable composite web; and

(6) passing the thermoformable composite web through a thermoforming section to provide a thermoformed article.

19. The process of claim 18, which comprises the further steps of:

(7) removing excess material from the thermoformed article; and



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(8) recycling the removed excess material.

20. A substantially bio-based biodegradable article with improved mechanical properties obtainable by means of the process according to claim 16.



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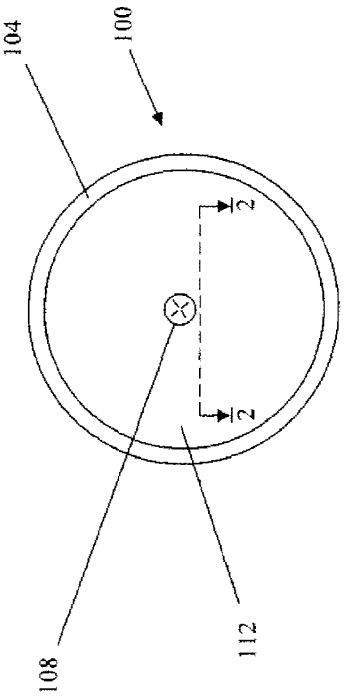



FIG. 1

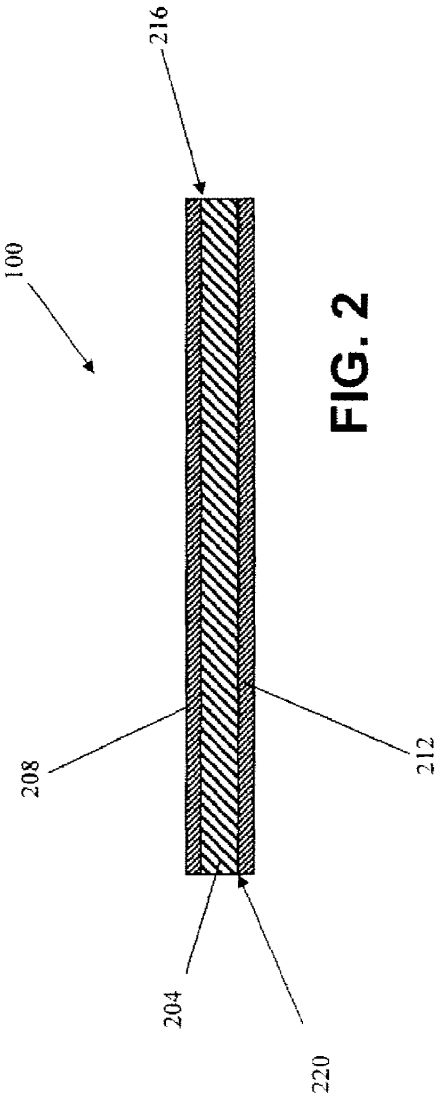
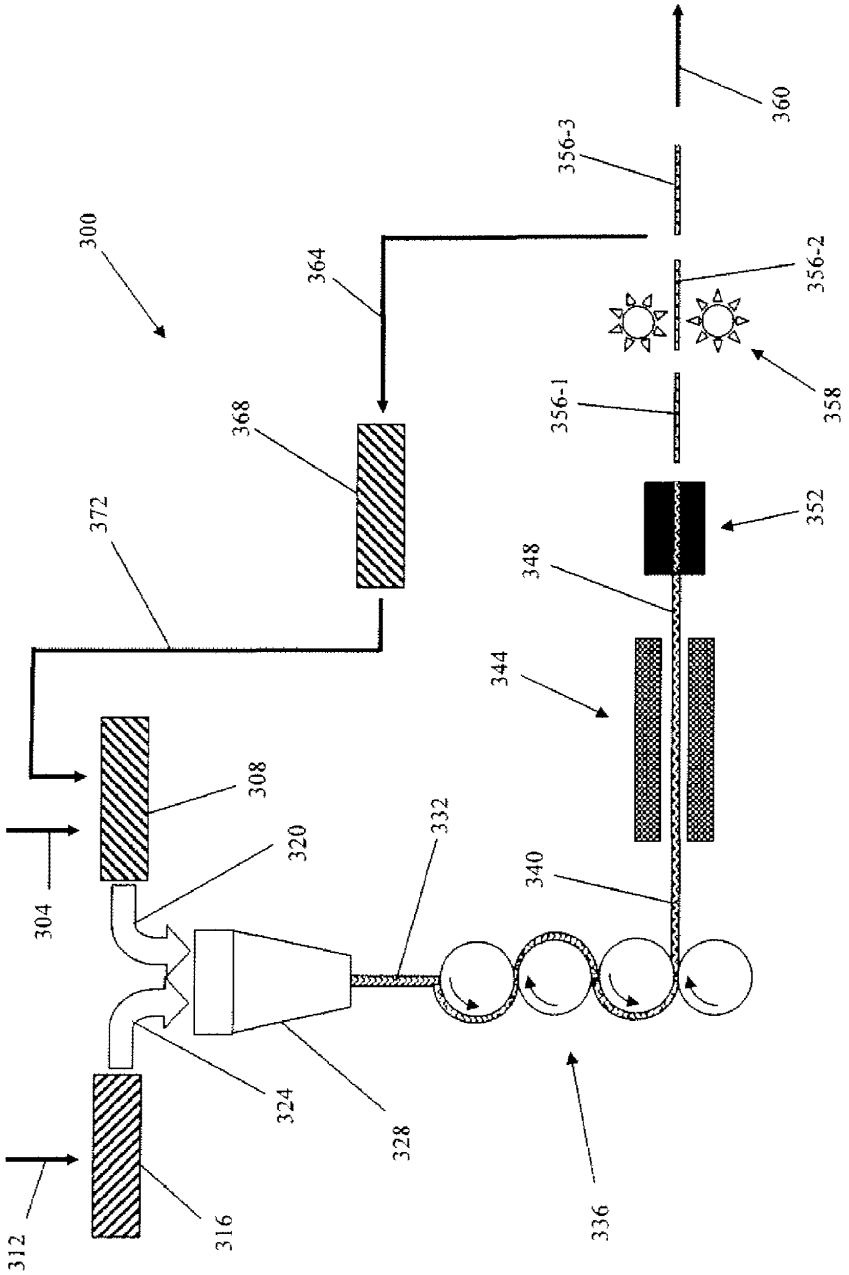



FIG. 2



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FIG. 3






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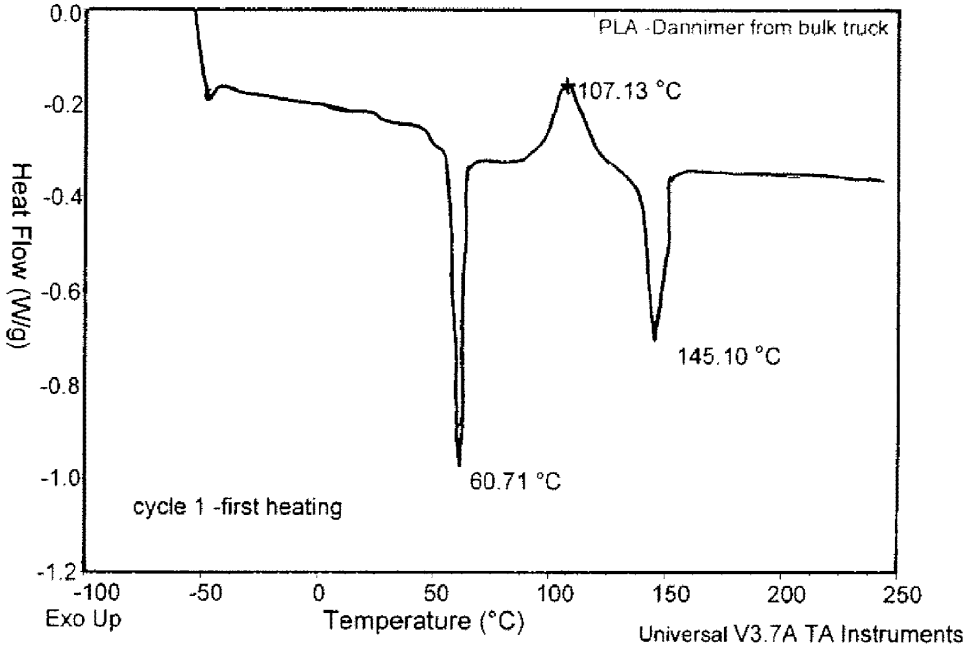



FIG. 4



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4/5

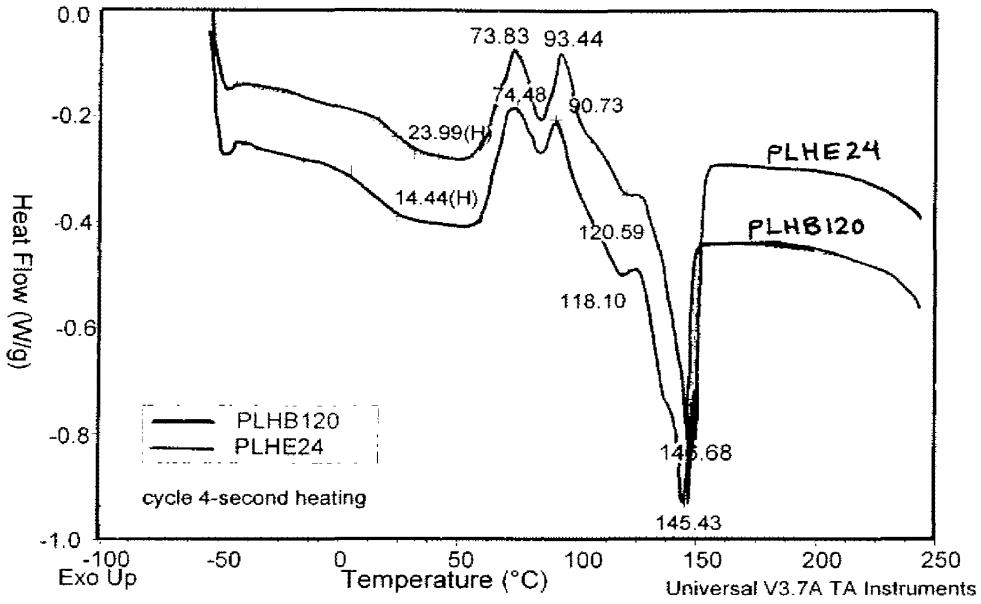



FIG. 5



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5/5

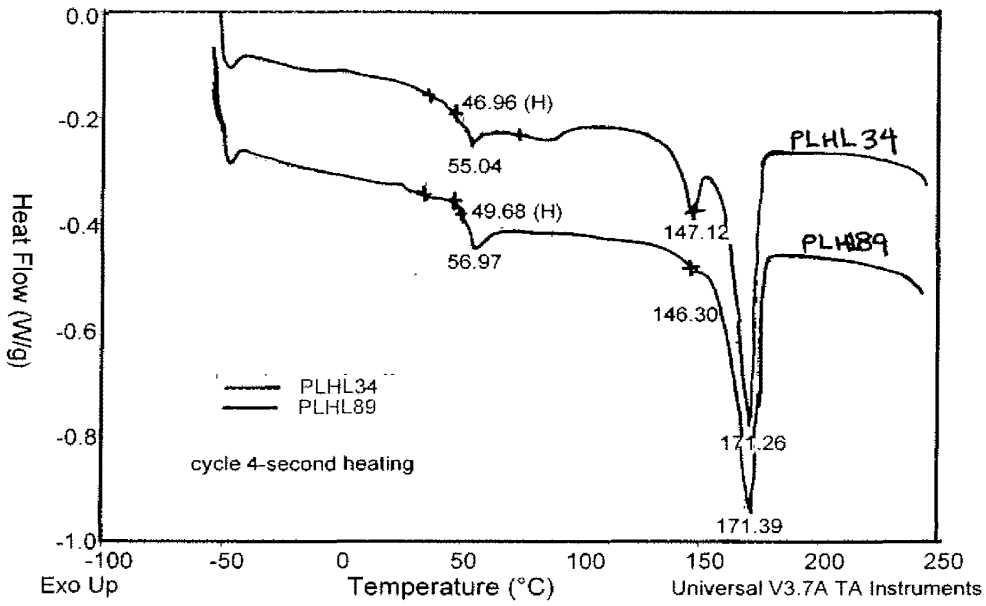



FIG. 6



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# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/042662

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. B32B9/02 B32B27/08 B32B27/36 B65D1/28 C08J5/04
C08L101/16

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)
B32B B65D C08J C08L

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,Y | EP 1 541 345 A (MITSUBISHI PLASTICS INC [JP]) 15 June 2005 (2005-06-15) paragraphs [0002] - [0006] paragraphs [0001], [0014], [0015], [0017], [0019], [0032], [0052] ----- | 1-11, 16-20 |
| X,Y | DATABASE WPI Week 200815 Thomson Scientific, London, GB; AN 2008-C01878 XP002536587 -& JP 2008 030332 A (MITSUI CHEM INC) 14 February 2008 (2008-02-14) abstract ----- -/-- | 1-11, 16-20 |

[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

"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

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 28 August 2009 | 07/09/2009 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Schambeck, Werner |

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X,Y | DATABASE WPI Week 200825<br>Thomson Scientific, London, GB; AN<br>2008-D42598<br>XP002536588<br>-& JP 2008 055694 A (KYODO PRINTING CO<br>LTD) 13 March 2008 (2008-03-13)<br>abstract | 1-11,<br>16-20 |
| Y | US 2007/092745 A1 (NIE LI [US] ET AL)<br>26 April 2007 (2007-04-26)<br>paragraphs [0002], [0003], [0005],<br>[0006], [0009] | 1-11,<br>16-20 |
| X | | 12-15 |
| Y | DATABASE WPI Week 200821<br>Thomson Scientific, London, GB; AN<br>2008-C78265<br>XP002536572<br>-& CN 101 003 667 A (DONGLI FIBRIN RES<br>INST CO LTD) 25 July 2007 (2007-07-25)<br>abstract | 1-11,<br>16-20 |
| X | | 12-15 |
| X | EP 1 630 195 A (SONY CORP [JP])<br>1 March 2006 (2006-03-01)<br>paragraphs [0002], [0010], [0011],<br>[0016], [0017], [0024], [0026], [0027] | 12-15 |
| X | DATABASE WPI Week 200708<br>Thomson Scientific, London, GB; AN<br>2007-078887<br>XP002543315<br>-& JP 2006 328138 A (MATSUSHITA ELECTRIC<br>WORKS LTD) 7 December 2006 (2006-12-07)<br>abstract | 12-15 |



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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2009/042662

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.



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**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11 and 16-20 relating to

   a thermoformable composite comprising a renewable polymer and/or natural fiber core and a heat-resistant polymer outer layer

   ---

2. claims: 12-15 relating to

   a thermoformable composite comprising a single layer containing a renewable polymer and natural fillers

   ---

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/042662

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 1541345 A | 15-06-2005 | AU 2003248270 A1 | 02-02-2004 |
| | | WO 2004007197 A1 | 22-01-2004 |
| | | US 2006040119 A1 | 23-02-2006 |
| JP 2008030332 A | 14-02-2008 | NONE | |
| JP 2008055694 A | 13-03-2008 | NONE | |
| US 2007092745 A1 | 26-04-2007 | NONE | |
| CN 101003667 A | 25-07-2007 | NONE | |
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| | | JP 4270072 B2 | 27-05-2009 |
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| | | US 2006047026 A1 | 02-03-2006 |
| JP 2006328138 A | 07-12-2006 | NONE | |

Form PCT/ISA/210 (patent family annex) (April 2005)

| Electronic Patent Application Fee Transmittal | |
|---|---|
| **Application Number:** | 11348150 |
| **Filing Date:** | 06-Feb-2006 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Attorney Docket Number:** | FDS-029388-US |
| Filed as Large Entity | |

**Utility under 35 USC 111(a) Filing Fees**

| 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:** | | | | |
| **Extension-of-Time:** | | | | |

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Miscellaneous:** | | | | |
| Submission- Information Disclosure Stmt | 1806 | 1 | 180 | 180 |
| | | **Total in USD ($)** | | **180** |

| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 9768776 |
| **Application Number:** | 11348150 |
| **International Application Number:** | |
| **Confirmation Number:** | 5681 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Customer Number:** | 01726 |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Filer Authorized By:** | Matthew M. Eslami |
| **Attorney Docket Number:** | FDS-029388-US |
| **Receipt Date:** | 30-MAR-2011 |
| **Filing Date:** | 06-FEB-2006 |
| **Time Stamp:** | 09:15:44 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| | |
|---|---|
| Submitted with Payment | yes |
| Payment Type | Deposit Account |
| Payment was successfully received in RAM | $180 |
| RAM confirmation Number | 7805 |
| Deposit Account | 090525 |
| Authorized User | |
| The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:<br>Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees)<br>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 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance 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 | Information Disclosure Statement (IDS) Filed (SB/08) | 110330_ids_fds029388us.pdf | 612710<br>c2c60f6f967c7487ddf37b41f19028f67b083d4f | no | 5 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 2 | | 110330_foreignref_fds029388us.pdf | 8433908<br>4f942374bbc2411a4d4a2ef4830c7a386cc206bf | yes | 193 |

**Multipart Description/PDF files in .zip description**

| Document Description | Start | End |
|---|---|---|
| Foreign Reference | 1 | 12 |
| Foreign Reference | 13 | 25 |
| Foreign Reference | 26 | 40 |
| Foreign Reference | 41 | 50 |
| Foreign Reference | 51 | 65 |
| Foreign Reference | 66 | 81 |
| Foreign Reference | 82 | 89 |
| Foreign Reference | 90 | 152 |
| Foreign Reference | 153 | 193 |

| | | | | | |
|---|---|---|---|---|---|
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 3 | Fee Worksheet (PTO-875) | fee-info.pdf | 30328<br>847a1a6649b3e4d69e89d032dc41b8c84cda0441 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 9076946 | | |

**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.**

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
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 displays a valid OMB control number.

# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | ☐ To be Mailed |
|---|---|---|
| 11/348,150 | 02/06/2006 | |

## APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY ☐ RATE ($) | SMALL ENTITY ☐ FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY FEE ($) |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | | | | | |
| ☐ BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | 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 $250 ($125 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 | | | TOTAL | |

## APPLICATION AS AMENDED – PART II

AMENDMENT 03/30/2011

| | (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)) | * 13 | Minus | ** 73 | = 0 | X $ = | | OR | X $52= | 0 |
| Independent (37 CFR 1.16(h)) | * 2 | Minus | ***13 | = 0 | X $ = | | OR | X $220= | 0 |
| ☐ 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 | 0 |

AMENDMENT

| | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| 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 number found in the appropriate box in column 1.

Legal Instrument Examiner:
/ANNIE c. SINGLETON/

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.*

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. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 04/14/2011

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
LOVELAND, OH 45140

| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 04/14/2011 | PAPER |

**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.

| Office Action Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 11/348,150 | CLEVELAND ET AL. | |
| | Examiner | Art Unit | |
| | MARC A. PATTERSON | 1782 | |

*-- 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* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, 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 *30 March 2011*.

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

3)☐ 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**

4)☒ Claim(s) *74-84,87 and 88* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *74-84,87 and 88* is/are rejected.

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

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

**Application Papers**

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

10)☐ 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).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**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).

a)☐ All b)☐ Some * c)☐ None of:

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) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *3/30/11*.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

## DETAILED ACTION

### WITHDRAWN REJECTIONS

1. The 35 U.S.C. 102(b) rejection of Claims 74, 81 – 83 and 85 – 88 as being anticipated by Asrar et al. (U.S. Patent No. 6,025,028), of record on page 2 of the previous Action, is withdrawn.

### NEW REJECTIONS

**Claim Rejections – 35 USC § 102(b)**

2. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

3. Claims 76 - 78 and 80 are rejected under 35 U.S.C. 102(b) as being anticipated by Doane et al. (U.S. Patent No. 6,040,063).

With regard to Claim 76, Doane et al discloses a laminate comprising substrate comprising a substrate (column 4, lines 32 - 39) and an interior and exterior moisture protective layer (coating '16' in Figure 2; column 4, lines 29 - 31) comprising biodegradable polyester (column 4, line 52).

With regard to Claims 77 - 78 and 80, Doane et al discloses polyester comprising polyhydroxyalkanoate (column 10, line 42) and a filler comprising calcium carbonate (column 9, line 41).

**Claim Rejections – 35 USC § 103(a)**

4. The following is a quotation of 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.

5. Claims 74 – 75, 81 – 88 are rejected under 35 U.S.C. 103(a) as being unpatentable over Asrar et al (U.S. Patent No. 6,025,028) in view of Lind et al (U.S. Patent 4,267,960).

With regard to Claim 74, Asrar et al discloses a laminate comprising a substrate (paper bag; column 10, line 59 - 61) having a heat - sealable coating (column 10, lines 59 - 61), therefore an interior layer, which is a moisture protective layer comprising biodegradable polyester (column 1, line 7 - 11). Asrar et al fail to disclose a substrate in the form of a cup.

Lind et al disclose a substrate in the form of a cup (bag structure shown in Figure 1) for the purpose of obtaining a substrate for packaging meat (column 3, lines 22 - 23).

It therefore would have been obvious for one of ordinary skill in the art to provide for a substrate in the form of a cup in order to obtain a packaging for meat as taught by Lind et al.

With regard to Claims 75 and 84, Asrar et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Asrar et al discloses layers comprised in a cup, as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

With regard to Claims 81 - 83 and 87 - 88, Asrar et al discloses polyester comprising polyhydroxyalkanoate (column 10, line 54 - 55) and a filler comprising calcium carbonate (column 8, lines 59 - 60).

With regard to Claims 85 - 86, the laminate is a cup (tray; column 10, lines 59 - 61).

6. Claim 79 is rejected under 35 U.S.C. 103(a) as being unpatentable over Doane et al. (U.S. Patent No. 6,040,063).

Doane et al disclose a laminate as discussed above. Doane et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Doane et al discloses layers comprised in a tray (column 4, lines 10 - 13), as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

## ANSWERS TO APPLICANT'S ARGUMENTS

7. Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 74, 81 – 83 and 85 – 88 as being anticipated by Asrar et al. (U.S. Patent No. 6,025,028), of record in the previous Action, have been considered and have been found to be persuasive. The rejection is therefore withdrawn. The new rejections above are directed to amended Claims 74, 81 - 83, and 85 - 88.

Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 76 - 78 and 80 as being anticipated by Doane et al. (U.S. Patent No. 6,040,063), of record in the previous

Action, have been considered but have not been found to be persuasive for the reasons set forth below.

Applicant argues, on page 10 of the remarks dated March 30, 2011 that two distinct and separate moisture barrier layers are not disclosed by Doane et al.

However, Figure 2 clearly shows two separate and distinct layers, 14 and 16, which are moisture barrier layers.

Applicant also argues, on page 11, that Doane is not in the form of a cup.

However, Doane has an inner surface with walls, as shown in Figure 1, and is therefore a cup.

Applicant also argues on page 11 that a filler comprising calcium carbonate is not disclosed by Doane, although Doane discloses calcium carbonate.

However, because Doane discloses calcium carbonate, Doane discloses calcium carbonate that at least partially fills the polyester of Doane. Furthermore, it is unclear why the calcium carbonate disclosed by Doane would fail to provide the properties provided by the claimed calcium carbonate.

Applicant also argues, on page 15, that there is nothing in Doane to factually support why one of ordinary skill in the art would select the claimed coat weight.

However, because the weight of Doane is dependent on the weight of the layers, in the absence of unexpected results it would have been obvious for one of ordinary skill in the art to select the claimed coat weight, or a different coat weight, depending on the desired use of the end product.

8. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497. The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Rena Dye can be reached on 571-272-1498. 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).

/Marc A Patterson/
Primary Examiner, Art Unit 1782

| Notice of References Cited | Application/Control No. 11/348,150 | Applicant(s)/Patent Under Reexamination CLEVELAND ET AL. | |
|---|---|---|---|
| | Examiner MARC A. PATTERSON | Art Unit 1782 | Page 1 of 1 |

**U.S. PATENT DOCUMENTS**

| * | | Document Number Country Code-Number-Kind Code | Date MM-YYYY | Name | Classification |
|---|---|---|---|---|---|
| * | A | US-4,267,960 | 05-1981 | Lind et al. | 383/106 |
| | B | US- | | | |
| | 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 | Classification |
|---|---|---|---|---|---|---|
| | N | | | | | |
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| | R | | | | | |
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| | 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.



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
Page 652 of 1179

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

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

| | |
|---|---|
| Application Number | 11348150 |
| Filing Date | 2006-02-06 |
| First Named Inventor | CLEVELAND, CS |
| Art Unit | 1782 |
| Examiner Name | Patterson, Marc A. |
| Attorney Docket Number | FDS-029388-US |

**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 | | | | | |

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|---|---|---|---|---|---|---|
| /M.P./ | 1 | 20070092745 | | 2007-04-26 | Li Nie, et al | |

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| Examiner Initial* | Cite No | Foreign Document Number[3] | Country Code[2] i | 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] |
|---|---|---|---|---|---|---|---|---|
| /M.P./ | 1 | 101003667 | CN | | 2007-07-25 | Dongli Fiber Inst China co Ltd | | ☐ |
| /M.P./ | 2 | 1541345 | EP | | 2003-07-10 | Mitsubishi Plastics, Inc. | | ☐ |
| /M.P./ | 3 | 1630195 | EP | | 2005-08-16 | Sony Corporation | | ☐ |

| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
|---|---|---|
| | Application Number | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| /M.P./ | 4 | 2006328138 | JP | | 2006-12-07 | Matsushita Electric Works Ltd | | ☐ |
| /M.P./ | 5 | 200830332 | JP | | 2008-02-14 | Mitsui Chemicals Inc. | | ☐ |
| /M.P./ | 6 | 1644794 | CN | | 2005-07-27 | Changchun Applied Chemistry | | ☐ |
| /M.P./ | 7 | 2394779 | CN | | 2000-09-06 | Chao Zaizhao | | ☐ |
| /M.P./ | 8 | 2004106630 | WO | | 2004-12-09 | | | ☐ |
| /M.P./ | 9 | 2009137382 | WO | | 2009-11-12 | International Paper Company | | ☐ |

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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. | T5 |
|---|---|---|---|
| | 1 | | ☐ |

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**EXAMINER SIGNATURE**

| Examiner Signature | /Marc Patterson/ | Date Considered | 04/11/2011 |
|---|---|---|---|

*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.

| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
|---|---|---|
| | Application Number | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

[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.

Docket No.: FDS-029388-US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

| | | |
|---|---|---|
| CLEVELAND, et al. | : | GROUP ART UNIT: 1782 |
| SERIAL NO: 11/348,150 | : | EXAMINER: PATTERSON, MARC A. |
| FILED: February 06, 2006 | : | CONFIRMATION #: 5681 |

FOR: BIODEGRADABLE PAPER-BASED LAMINATE WITH OXYGEN AND MOISTURE BARRIER PROPERTIES AND METHOD FOR MAKING BIODEGRADABLE PAPER-BASED LAMINATE

**AMENDMENT**

United States Patent and Trademark Office
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In response to the Office Action (non-final) mailed April 14, 2011, the period for response which is set to expire July 14, 2011, please amend the above application as follows, as well as consider the following remarks.

Applicants' representative, Matthew M Eslami, also respectfully requests a telephone conference in the event the Examiner has any questions, comments or suggestions that would place any pending claim not in allowable form in better condition for allowance. Applicant's representative may be reached directly at 513-248-6193.

No extension of time is believed to be required. However, the Commissioner is hereby authorized by this paper to charge any fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment, to Deposit Account No. 09-0525.

**Amendments to/Listing of the Claims** begin on page **2** of this paper.

**Remarks/Arguments** begin on page **5** of this paper.

**IN THE CLAIMS**

The listing of claims will replace all prior versions, and listings, of claims in the application:

**Listing of Claims:**

Claims 1-73. (Canceled).

74. (Previously Presented) A product in the form of a cup comprising a laminate forming a moisture barrier, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface; and

a moisture protectant layer disposed solely on said interior surface of said substrate and comprising at least one biodegradable polyester polymer.

75. (Previously Presented) The product laminate according to claim 74, wherein the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

76. (Previously Presented) A product in the form of a cup comprising a laminate forming moisture barriers, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface;

a first moisture barrier layer disposed on said interior surface of said substrate; and

a second moisture protectant layer disposed on said exterior surface of said substrate and comprising at least one biodegradable polyester polymer, wherein the second moisture barrier layer is separate from the first moisture barrier layer disposed on said interior surface of said substrate.

77. (Currently Amended) The product according to Claim 88, wherein the second moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler.

78. (Currently Amended) The product according to Claim 77, wherein the second moisture protectant layer comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

79. (Previously Presented) The product according to claim 76, wherein the second moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

80. (Currently Amended) The product according to Claim 76, wherein the second moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate and starch.

81. (Currently Amended) The product according to Claim 87, wherein the moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler.

82. (Currently Amended) The product according to 81, wherein the moisture protectant layer comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

83. (Currently Amended) The product according to Claim 74, wherein the moisture protectant layer further comprises from 5 to 20 percent by weight of at least one member selected from the group consisting of calcium carbonate and starch.

84. (Currently Amended) The product according to Claim 74, wherein the substrate comprises paperboard; and the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$ and comprises polylactic acid and from 5 to 20 percent by weight of at least one member selected from the group consisting of calcium carbonate and starch.

85-86 (Cancelled).

87. (Previously Presented) The product according to claim 74, wherein the at least one biodegradable polyester polymer is selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

88. (Previously Presented) The product according to claim 76, wherein the second moisture protectant layer comprises at least one biodegradable polyester polymer selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

## REMARKS/ARGUMENTS

### A. Status of Claims

Favorable reconsideration of this application is respectfully requested. Claims 1-73 and 85-86 have previously been cancelled. Claims 74-84 and 87-88 are currently pending.

### B. Procedural Matters

Applicants gratefully acknowledge the Examiner's statements at pages 2 and 4 of the present Office Action that the prior rejection of Claims 74, 81-83 and 87-88 under 35 U.S.C. § 102(b) as being anticipated by U.S. Pat. No. 6,025,028 to Asrar et al (hereafter referred to as "**Asrar**") has been withdrawn in view of the persuasiveness of Applicants' arguments in their prior amendment after final of March 30, 2011 (hereafter referred to as "March 30, 2011 AAF").

### C. Amendments to Claims

Claims 77-78 and 81-82 have each been amended to recite that the respective moisture protect layers comprise **from 5 to 20 percent by weight** of the at least one filler. Support for these amendments to Claims 77-78 and 81-32 74 may be found, for example, in paragraph [0016] of the present application.

Similar to amended Claims 78-79 and 81-82, Claims 83-84 have each been amended to recite that the respective moisture protectant layer comprises **from 5 to 20 percent by weight** of the at least one member selected from the group consisting of calcium carbonate and starch. Support for these amendments to Claims 83-84 may also be found, for example, in paragraphs [0016] and [0051] of the present application.

### D. Response to Rejection of Claims 76-78 and 80 under 35 U.S.C. § 102(b) as Being Anticipated by Doane

At page 2 of the present Office Action, Claims 76-78 and 80 have been rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Pat. No. 6,040,063 to Doane et al. (hereafter referred to as (hereafter referred to as "**Doane**"). **This rejection is respectfully traversed with respect to these Claims**, as amended or as currently presented, for at least the following reasons.

In support of the rejection of Claim 76 as being anticipated by **Doane**, the present Office Action makes the following allegation:

> ***Allegation 1***: [**Doane**] discloses a laminate comprising [a] substrate (column 4, lines 32-39) and **an interior and exterior moisture protective layer** (coating '16' in Figure 2; column 4, lines 29-31) comprising [a] biodegradable polyester (column 4, line 52).[1]

What Allegation 1 asserts does not support the rejection of Claim 76 as anticipated by **Doane**. Claim 76 is distinguishable over **Doane** in reciting that the second moisture barrier layer of the laminate of the cup, which is disposed on the exterior substrate surface, **is separate from the first moisture barrier layer disposed on the interior substrate surface**. In other words, Claim 76 recites **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate**. By contrast, and contrary to what Allegation 1 asserts, coating layer 16 of **Doane** forms only **one continuous and surrounding exterior layer** with respect structure 12. In fact, and contrary to the requirements of 37 CFR § 1.104(c)(2)[2] and MPEP § 707.05,[3] Allegation 1 provides an **inadequate explanation** as to how **Doane** teaches **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to amended Claim 76.

In response to Applicants' argument at page 10 of their prior March 30, 2011 AAF that **Doane** does not disclose two separate and distinct moisture barrier layers, one each disposed on the interior and exterior surface of the substrate, page 5 of the present Office Action makes the following additional allegation:

> ***Allegation 2***: However, Figure 2 [of **Doane**] clearly shows **two separate and distinct layers, 14 and 16**, which are moisture barrier layers.[4]

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[1] See page 2 of the present Office Action (emphasis added).
[2] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)
[3] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)
[4] See page 2 of the present Office Action (emphasis added).

What Allegation 2 asserts also does not support the rejection of Claim 76 as anticipated by **Doane**. Applicants agree that layers 14 and 16 shown in FIG. 2 of **Doane** are separate and distinct layers. But, again contrary to the requirements of 37 CFR § 1.104(c)(2)[5] and MPEP § 707.05,[6] what Allegation 2 neglects to address, and what is not shown by layers 14 and 16 in FIG. 2 of **Doane**, are one of each of these separate and distinct moisture barrier layers **being disposed on the interior and exterior surface of the substrate** as recited in Claim 76. Instead, layer 14 is disposed on interior layer 12 (which Allegation 1 characterizes as the "substrate"), while layer 16 is disposed on layer 14 (not interior layer 12). Like Allegation 1, Allegation 2 again **mischaracterizes** what is fairly taught by FIG. 2 of **Doane** with respect to the positioning of moisture barrier layers with respect to the interior and exterior surfaces of the substrate according to Claim 76.

If the Examiner still maintains that **Doane** teaches a **cup**[7] comprising a laminate having **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to Claim 76 based on what is asserted in Allegations 1-2, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 76 under 35 U.S.C. § 102(b) as being anticipated by **Doane** for the reasons presented in Allegations 1-2, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[8] because this rejection appears to be based, at

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[5] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[6] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

[7] Page 5 of the present Office Action also asserts that page 11 of Applicants' prior March 30, 2011 AAF argues that "[**Doane**] is not in the form of a cup." But that assertion **mischaracterizes** what was said at page 11 of Applicants' prior March 30, 2011 AAF. Applicants' primary emphasis in their argument at page 11 of their prior March 30, 2011 AAF was on **Doane** not teaching a laminate having **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to Claim 76. In addition, the further assertion at page 5 of the present Office Action that **Doane**, because FIG. 1 shows "an inner surface with walls," "is therefore a cup" again **mischaracterizes** what even **Doane** identifies element 10 to be (a "foam tray"). See, for example, column 3, lines 56-57. In fact, nowhere does **Doane** even mention that its structure can be a cup according to Claim 76.

[8] See 37 CFR § 1.104(d)(2) which states: "When a rejection in an application is based on facts within the personal knowledge of an employee of the Office, the data shall be as specific as possible, and the reference must be supported, when called for by the applicant, by the affidavit of such employee, and such affidavit shall be subject to

least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 77-78 and 80 as being anticipated by **Doane**, the present Office Action makes the following allegation:

> ***Allegation 3***: [**Doane**] discloses [a] polyester comprising polyhydroxyalkanoate (column 10, line 42) and a **filler** comprising calcium carbonate (column 9, line 41).[9]

What Allegation 3 asserts also does not support the rejection of Claims 77-78 and 80, as amended, as being anticipated by **Doane**. Amended Claims 77-78 and 80 depend, directly or indirectly, from Claim 76. Accordingly, Amended Claims 77-78 and 80 are patentable over **Doane** for at least the same reasons presented above in response to Allegations 1-2, for why Claim 76 is patentable over this reference.

In addition, Claims 77-78 and 80 are further distinguishable over **Doane** in reciting that the moisture protectant layer comprises **at least one filler** which may be calcium carbonate (see amended Claims 78 and 80). First, and contrary to the requirements of 37 CFR § 1.104(c)(2)[10] and MPEP § 707.05,[11] Allegation 3 has **mischaracterized** what is fairly taught by **Doane** with regard to the use of calcium carbonate. Contrary to what Allegation 3 asserts, **Doane** does not teach that calcium carbonate is being used as a filler according to amended Claims 77-78 and 80.

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contradiction or explanation by the affidavits of the applicant and other persons." Applicants note that in the unpublished case of *In re Sun*, 31 USPQ2d 1451, 1455 (Fed. Cir. 1993), the USPTO argued "the procedures established by 37 C.F.R. Section 1.107(b) (1993) [now 37 CFR § 1.104(d)(2)] ***expressly entitle*** an Applicant, on mere request, to an examiner affidavit that provides [citations that support the Examiner's asserted level of skill in the art]" (emphasis added). Furthermore, in *In re Sun*, the Federal Circuit, held that "this procedure, so readily available, helps save the lack of citation in an office action from possible constitutional infirmity in denying reasonable notice and hence due process." See 31 USPQ2d at 1455. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 18): "If it is not possible for the examiner to provide this type of information, **the examiner might choose instead to provide an affidavit detailing the examiner's own personal knowledge** (as a person approximating one of ordinary skill in the art) of the technology in question (citing 37 CFR § 1.104(d)(2)) (emphasis added)."

[9] See page 3 of the present Office Action (emphasis added).

[10] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[11] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

Instead, **Doane** teaches that calcium carbonate is being used as a "nucleating agent" for a foamable composition.[12]

Second, these "nucleating agents" are taught by **Doane** for use **in preparing natural polymer foams for structure 12**,[13] and not hydroxyfunctional polyester layer 14 which is self-adhered **to the exterior surface** of structure 12. In other words, and contrary to what Allegation 3 asserts, **Doane** does not teach inclusion of calcium carbonate (or any other disclosed "nucleating agent") in its hydroxyfunctional polyester layer 14 (or layer 16), much less the moisture protectant layers of amended Claims 77-78 and 80. In fact, the Examiner previously agreed at an November 29, 2010 Interview[14] that **Doane** does not teach inclusion of calcium carbonate or any other "filler" in the moisture protectant layers of amended Claims 77-78 and 80.

In response to Applicants' argument at page 11 of their prior March 30, 2011 AAF that **Doane** does not disclose two separate and distinct moisture barrier layers, one each disposed on the interior and exterior surface of the substrate, page 5 of the present Office Action makes the following additional allegation:

> ***Allegation 4***: However, because [**Doane**] discloses calcium carbonate, [**Doane**] discloses calcium carbonate **that at least partially fills the polyester** of [**Doane**]. Furthermore, it unclear why the calcium carbonate disclosed by [**Doane**] **would fail to provide the properties provided by the claimed calcium carbonate**.[15]

What Allegation 4 asserts also does not support the rejection of amended Claims 77-78 and 80 as anticipated by **Doane**. Like Allegation 3, and contrary to the requirements of 37 CFR § 1.104(c)(2)[16] and MPEP § 707.05,[17] what Allegation 4 asserts **mischaracterizes** what **Doane** teaches concerning the use of calcium carbonate (i.e., as a "nucleating agent" for a foamable composition). But more significantly, in asserting that the calcium carbonate of **Doane** "at least

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[12] See column 9, lines 33-41, of **Doane**.
[13] See, for example, column 7, lines 53-56, and column 9, lines 4-6, of **Doane**.
[14] See page 9 of Applicants' prior amendment of December 10, 2010.
[15] See page 2 of the present Office Action (emphasis added).
[16] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)
[17] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

partially fills the polyester," Allegation 4 completely ignores and further mischaracterizes **where Doane** positions this calcium carbonate "nucleating agent." Contrary to what Allegation 4 suggests, the "polyester" referred to in Allegation 4 is again the polymer foam for structure 12, and not the hydroxyfunctional polyester layer 14 (or layer 16) of **Doane**, much less the moisture protectant layers of amended Claims 77-78 and 80.

In further response to what Allegation 4 erroneously asserts, Claims 77-78 and 80 have been amended to recite that the "at least one filler" (e.g., calcium carbonate) comprises **from 5 to 20 percent by weight** of the respective moisture protectant layer. Nowhere does **Doane** teach that its foamable polymers comprise this recited amount of these "nucleating agents." In fact, nowhere does **Doane** mention **any amount** for these "nucleating agents."

If the Examiner still maintains that **Doane** teaches **at least one filler** in the moisture protectant layer **in an amount of from 5 to 20 percent weight** according to amended Claims 77-78 and 80 based on what is asserted in Allegations 3-4, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 77-78 and 80 under 35 U.S.C. § 102(b) as being anticipated by **Doane** for the reasons presented in Allegations 3-4, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claims 76-78 and 80, as amended or as currently presented, are patentable over **Doane**. Accordingly, the rejection of these Claims under 35 U.S.C. § 102(b) based on this reference should be withdrawn.

**E. Response to Rejection of Claims 74-75, 81-83, and 87-88 under 35 U.S.C. § 103(a) as Being Unpatentable over Asrar, in view of Lind**

At pages 3-4 of the present Office Action, Claims 74, 81-83, and 87-88[18] have been rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Pat. No. 6,025,028 to Asrar et al (hereafter referred to as "**Asrar**"), in view of U.S. Pat. No. 4,267,960 to Lind et al. (hereafter referred to as "**Lind**"). **This rejection is respectfully traversed with respect to Claims**, as amended or as currently presented, for at least the following reasons.

In support of the rejection of Claim 74 as being unpatentable over **Asrar**, in view of **Lind**, page 3 of the present Office Action makes the following allegations:

> ***Allegation 5***: [**Asrar**] discloses a laminate comprising a substrate a substrate (paper bag; column 10, lines 59-61) having a heat-sealable coating, **therefore an interior layer**, which is a moisture protective layer comprising [a] biodegradable polyester (column 1, lines 7-11). [**Asrar**] **fails to disclose a substrate in the form of a cup**.[19]
>
> ***Allegation 6***: [**Lind**] **disclose[s] a substrate in the form of a cup** (bag structure shown in Figure 1) for the purpose of obtaining a substrate for packaging meat (column 3, lines 22-23).[20]
>
> ***Allegation 7***: It therefore would have been obvious to one of ordinary skill in the art to provide for a substrate in the form of a cup in order to obtain packaging for a meat as taught by [**Lind**].[21]

What Allegations 5-7 assert does not support the rejection of Claim 74 as unpatentable over **Asrar**, even in view of **Lind**. Claim 74 recites a **product in the form of a cup comprising** the laminate forming a moisture barrier, **said laminate** comprising a substrate having a separate interior product contacting surface and a separate exterior surface, wherein the moisture protectant layer is disposed solely on the interior surface of the substrate. Claim 74 is therefore distinguishable over the teachings of **Asrar** at least with respect to the following features: (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**; (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate.

Contrary to what Allegation 5 asserts, **Asrar** does not teach that its coating (1) is on the

[18] Claims 85 and 86 have previously been cancelled, so the reference of this rejection to those Claims is moot.
[19] See pages 3 of the present Office Action (emphasis added).
[20] See pages 3 of the present Office Action (emphasis added).
[21] See page 3 of the present Office Action (emphasis added).

interior surface of the substrate when in the form of a cup, and especially (2) is solely on the interior surface of the substrate. Instead, all that **Asrar** says in column 10, lines 59-61, relied upon by Allegation 5 is that the "[p]referred objects suitable for coating" include "cups, paper, paper waste bags, etc." Nothing described in column 10, lines 59-61, of **Asrar** relied upon by Allegation 5 (or in any other portion of **Asrar**) can be construed as teaching features (1) or (2) of the cup recited in Claim 74. Instead, and contrary to the requirements of 37 CFR § 1.104(c)(2)[22] and MPEP § 707.05,[23] Allegation 5 **never properly explains** how the "heat-sealable coating" of **Asrar** can be considered to be disposed on the interior surface according to Claim 74.

What Allegation 6 asserts **mischaracterizes** what is fairly taught by **Lind**. Contrary to what Allegation 6 asserts, **Lind** does not teach a substrate in the form of a cup. Instead, as the portions (column 3, lines 22-23 ) of this reference relied upon by Allegation 6 clearly say, **Lind** teaches a "heat sealable meat packaging bag." In fact, and contrary to the requirements of 37 CFR § 1.104(c)(2)[24] and MPEP § 707.05,[25] the basis in Allegation 6 for construing the "meat packaging bag" of **Lind** to be equivalent to the "cup" of Claim 74 is **never explained** and **completely absent** from the present Office Action.

Indeed, the basis asserted in Allegation 7 for combining **Lind** with **Asrar** is simply a "conclusory statement" that provides no "rational" explanation for why one of ordinary skill in the art would combine **Lind** with **Asrar** with respect to Claim 74. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[26] In fact, even if **Lind** were combined with **Asrar**, Allegation 7 does not explain

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[22] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[23] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

[24] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[25] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

26 *See e.g., In re Kahn,* 78 U.S.P.Q.2d 1329, 1336 (Fed. Cir. 2006)(emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id*. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight.

how **Lind** supplies features (1) and (2) of Claim 74 which Applicants have asserted above in response to Allegation 5 to be missing from **Asrar**.

If the Examiner still maintains that **Asrar**, in view of **Lind**, teaches (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**, (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate according to amended Claim 74 based on what is asserted in Allegations 5-7, then Applicants assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 74 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, in view of **Lind**, for the reasons presented in Allegations 5-7, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 75 and 84 as being unpatentable over **Asrar**, in view of **Lind**, the present Office Action makes the following allegations:

> ***Allegation 8***: [**Asrar**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Asrar**] discloses layers comprised in a cup, as discussed above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[27]

What Allegation 8 asserts does not support the rejection of Claims 75 or 84 as being unpatentable over **Asrar**, for at least the following reasons. First, for at least the reasons

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[Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

[27] See page 3 of the present Office Action (emphasis added).

presented above in response to Allegations 5-7, Claim 74 is patentable over **Asrar**. Allegation 8 does not assert that those features of Claim 74 (i.e., a cup comprising a laminate having a moisture barrier layer **which is disposed solely on the interior product contacting surface**) which were asserted **to be missing from the teachings** of **Asrar** are now taught by that reference. Claims 75 and 84 also depend directly from Claim 74, and are therefore patentable over **Asrar** (even in view of **Lind**) for at least the same reasons presented above in response to Allegations 5-7 for why Claim 74 is patentable over this reference.

Second, Allegation 8 concedes that the coat weights (not **thickness** as asserted in Allegation 8) recited in amended Claims 75 and 84 are not taught by **Asrar**. Instead, Allegation 8 asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually unsupported** by **Asrar**, the reference primarily relied upon in rejecting Claims 75 and 84. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[28]

Allegation 8 points to **absolutely nothing** in **Asrar** (or any other verifiable evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in Claims 75 and 84. In fact, it again appears that the Examiner is rejecting Claims 75 and 84 as being unpatentable over **Asrar**, even in view of **Lind**, based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claims 75 and 84 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, even in view of **Lind**, for the reasons

[28] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id.* See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discussing the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

presented in Allegation 8, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, **Lind**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 81-83, and 87-88 as being as being unpatentable over **Asrar**, in view of **Lind**, the present Office Action makes the following allegation:

> ***Allegation 9***: [**Asrar**] discloses [a] polyester comprising polyhydroxyalkanoate (column 10, line[s] 54-55) and a **filler** comprising calcium carbonate (column 8, lines 59-60).[29]

What Allegation 9 asserts also does not support the rejection of amended Claims 81-83 and Claims 87-88 as being unpatentable over **Asrar**, even in view of **Lind**. Amended Claims 81-83 and Claim 87 depend, directly or indirectly, from Claim 74. Accordingly, amended Claims 81-83 and Claim 87 are patentable over **Asrar** for at least the same reasons presented above in response to Allegations 5-7 for why Claim 74 is patentable over this reference, even in view of what **Lind** teaches.

In addition, amended Claims 81-83 are further distinguishable over **Asrar**, even in view of **Lind**, in reciting that the moisture protectant layer comprises **at least one filler** which may be calcium carbonate (see amended Claim 82). First, Allegation 9 has **mischaracterized** what is fairly taught by **Asrar** with regard to the use of calcium carbonate. Contrary to what Allegation 9 asserts, **Asrar** does not teach that calcium carbonate is being used as a filler according to amended Claims 81-83. Instead, **Asrar** teaches inorganic compounds such as metal oxides, metal hydroxides, and metal carbonates, preferably of metals such as aluminum, antimony, tin, sodium, calcium, magnesium, barium or zinc, "can be used to further improve nucleation activity and/or reduce the extent of discoloration and/or improve the clarity of PHA-derived products when used in combination" with ODPA nucleants to form **Asrar's** coating comprising the PHAs.[30] Nothing in **Asrar** suggests that calcium carbonate is being used as a filler according to

[29] See page 3 of the present Office Action (emphasis added).
[30] See column 8, lines 53-63, of **Asrar**.

amended Claims 81-83.

In further response to what Allegation 9 erroneously asserts, Claims 81-83 have been amended to recite that the "at least one filler" (e.g., calcium carbonate) comprises **from 5 to 20 percent by weight** of the respective moisture protectant layer. **Asrar** teaches that its "metal oxides, metal hydroxides, and metal carbonates" may be used with the ODPA nucleants in an amount of from 0.001 to 5 parts (most preferably from about 0.01 to 0.5 parts) per hundred parts of the PHA resin.[31] But **Asrar** also teaches that the ODPA nucleants may be used in an amount of from 0.01 to 5 parts (most preferably from about 0.02-0.5 parts) per hundred parts of the PHA resin.[32] Accordingly, given that **Asrar** does not teach what amounts of these "metal carbonates" should be used with what amounts of these ODPA nucleants, one of ordinary skill in this art would have no basis from this reference for selecting the amounts of "filler" recited in amended Claims 81-83.

If the Examiner still maintains that **Asrar** teaches **at least one filler** in the moisture protectant layer **in an amount of from 5 to 20 percent weight** according to amended Claims 81-83 based on what is asserted in Allegation 9, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 81-83 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, even in view of **Lind**, for the reasons presented in Allegation 9, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, **Lind**, or any other verifiable evidence provided by the Examiner.

Claim 88 depends from Claim 76. But the present Office Action has not rejected Claim 76 as unpatentable over **Asrar**. Accordingly, like Claim 76, amended Claim 88 must also be patentable over **Asrar**, even in view of **Lind**.

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[31] See column 9, lines 1-8, of **Asrar**.
[32] See column 8, lines 43-45, of **Asrar**.

For at least the foregoing reasons, Claims 74-7, 81-84, and 87-88, as amended or as currently presented, are patentable over **Asrar**, even in view of **Lind**. Accordingly, the rejection of these Claims under 35 U.S.C. § 103(a) over this combination of references should be withdrawn.

**G. Response to Rejection of Claim 79 under 35 U.S.C. § 103(a) as Being Unpatentable over Doane**

At page 4 of the present Office Action, Claim 79 has been rejected under 35 U.S.C. § 103(a) as being unpatentable over **Doane**. **This rejection is respectfully traversed with respect to this Claim**, as currently presented, for at least the following reasons.

In support of the rejection of Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane**, the present Office Action makes the following allegation:

> ***Allegation 10***: [**Doane**] discloses a laminate as discussed above. [**Doane**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Doane**] discloses layers comprised in a tray (column 4, lines 10-13), as discussed above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[33]

What Allegation 10 asserts does not support the rejection of Claim 79 as being unpatentable over **Doane** for at least the following reasons. First, for at least the reasons presented above in response to Allegations 1-2, Claim 76 is patentable over **Doane**. Allegation 10 does not assert that those features in Claim 76 (i.e., the second moisture barrier layer disposed on the exterior substrate surface **is separate from the first moisture barrier layer disposed on the interior substrate surface**) which were asserted **to be missing from the teachings** of **Doane** are now taught by that reference. Claim 79 also depends directly from Claim 76, and is therefore patentable over **Doane** for at least the same reasons presented above in response to Allegations 1-2 for why Claim 76 is patentable over this reference.

[33] See page 4 of the Final Action (emphasis added).

Second, Allegation 10 concedes that the coat weights (not **thickness** as asserted by Allegation 10) recited in amended Claim 79 are not taught by **Doane**. Instead, Allegation 7 asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion again amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually unsupported** by **Doane**, the reference relied upon in rejecting amended Claim 79. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[34]

Allegation 10 points to **absolutely nothing** in **Doane** (or any other verifiable evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in Claim 79. In fact, it again appears that the Examiner is rejecting Claim 79 as being unpatentable over **Doane** based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane** for the reasons presented in Allegation 10, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2) because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claim 79, as currently presented, is patentable over **Doane**. Accordingly, the rejection of this Claim under 35 U.S.C. § 103(a) over this reference should be withdrawn.

---

[34] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id.* See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discussing the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

**H. Conclusion**

Claims 74-84 and 87-88, as amended or as currently presented, are patentable over the art relied upon in the present Office Action. Accordingly, Claims 74-84 and 87-88 are in condition for allowance, and favorable action is earnestly solicited thereon.

Should the Examiner feel that there are any issues outstanding after consideration of this response, the Examiner is invited to contact Mr. Matthew M. Eslami at 513-248-6193 to expedite prosecution of the above application.

No extension of time is believed to be required. However, the Commissioner is hereby authorized by this paper to charge any fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment, to Deposit Account No. 09-0525. **This paragraph is intended to be a CONSTRUCTIVE PETITION FOR EXTENSION OF TIME in accordance with 37 C.F.R. § 1.136(a)(3) if needed.**

Respectfully Submitted,

Date: June 10, 2011

By: /Matthew M. Eslami/

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| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 10281037 |
| **Application Number:** | 11348150 |
| **International Application Number:** | |
| **Confirmation Number:** | 5681 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Customer Number:** | 01726 |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Filer Authorized By:** | Matthew M. Eslami |
| **Attorney Docket Number:** | FDS-029388-US |
| **Receipt Date:** | 10-JUN-2011 |
| **Filing Date:** | 06-FEB-2006 |
| **Time Stamp:** | 16:25:39 |
| **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 | | 110610_rsptooa_fds029388us.pdf | 188842<br>2d7cced9dccfd57b366c5f26a8231efc0adfc50e | yes | 19 |

| | Multipart Description/PDF files in .zip description | | |
|---|---|---|---|
| | **Document Description** | **Start** | **End** |
| | Amendment/Req. Reconsideration-After Non-Final Reject | 1 | 1 |
| | Claims | 2 | 4 |
| | Applicant Arguments/Remarks Made in an Amendment | 5 | 19 |
| **Warnings:** | | | |
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| | **Total Files Size (in bytes):** | 188842 | |

**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.**

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
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# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | ☐ To be Mailed |
|---|---|---|
| 11/348,150 | 02/06/2006 | |

## 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 | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | 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 $250 ($125 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 | | | TOTAL | |

## APPLICATION AS AMENDED – PART II

| AMENDMENT 06/10/2011 | (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)) | * 13 | Minus | ** 73 | = 0 | X $ = | | OR | X $52= | 0 |
| Independent (37 CFR 1.16(h)) | * 2 | Minus | ***13 | = 0 | X $ = | | OR | X $220= | 0 |
| ☐ 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 | 0 |

| AMENDMENT | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| 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 number found in the appropriate box in column 1.

Legal Instrument Examiner:
/YOLANDA A. MIDDLETON/

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.**

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 07/20/2011

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
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| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 07/20/2011 | PAPER |

**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.

| Office Action Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 11/348,150 | CLEVELAND ET AL. | |
| | Examiner | Art Unit | |
| | MARC PATTERSON | 1782 | |

*-- 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 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, 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 *10 June 2011*.

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

3)☐ 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**

4)☒ Claim(s) *74-84,87 and 88* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *74-84,87 and 88* is/are rejected.

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

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

**Application Papers**

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

10)☐ 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).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**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).

a)☐ All b)☐ Some * c)☐ None of:

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) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

## DETAILED ACTION

NEW REJECTIONS

### *Claim Rejections – 35 USC § 102(b)*

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

2. Claim 76 is rejected under 35 U.S.C. 102(b) as being anticipated by Doane et al. (U.S. Patent No. 6,040,063).

With regard to Claim 76, Doane et al discloses a laminate comprising substrate comprising a substrate (column 4, lines 32 - 39) and an interior and exterior moisture protective layer (coating '16' in Figure 2; column 4, lines 29 - 31) comprising biodegradable polyester (column 4, line 52).

### *Claim Rejections – 35 USC § 103(a)*

3. The following is a quotation of 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 74 - 75, 81 - 88 are rejected under 35 U.S.C. 103(a) as being unpatentable over Asrar et al (U.S. Patent No. 6,025,028) in view of Lind et al (U.S. Patent 4,267,960).

With regard to Claim 74, Asrar et al discloses a laminate comprising a substrate (paper bag; column 10, line 59 - 61) having a heat - sealable coating (column 10, lines 59 - 61), therefore an interior layer, which is a moisture protective layer comprising biodegradable polyester (column 1, line 7 - 11). Asrar et al fail to disclose a substrate in the form of a cup.

Lind et al disclose a substrate in the form of a cup (bag structure shown in Figure 1) for the purpose of obtaining a substrate for packaging meat (column 3, lines 22 - 23).

It therefore would have been obvious for one of ordinary skill in the art to provide for a substrate in the form of a cup in order to obtain a packaging for meat as taught by Lind et al.

With regard to Claims 75 and 84, Asrar et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Asrar et al discloses layers comprised in a cup, as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

With regard to Claims 81 - 83 and 87 - 88, Asrar et al discloses polyester comprising polyhydroxyalkanoate (column 10, line 54 - 55) and a filler comprising calcium carbonate (column 8, lines 59 - 60) in the amount of 5% by weight (column 9, line 7).

With regard to Claims 85 - 86, the laminate is a cup (tray; column 10, lines 59 - 61).

5. Claim 77 – 80 are rejected under 35 U.S.C. 103(a) as being unpatentable over Doane et al. (U.S. Patent No. 6,040,063).

Doane et al disclose a laminate as discussed above. With regard to Claims 77 – 78 and 80, Doane et al fail to disclose a calcium carbonate in the amount of 5 - 20% by weight. However, the calcium carbonate disclosed by Doane et al is for nucleation (column 9, lines 38 – 41). It therefore would have been obvious for one of ordinary skill in the art to select an amount of calcium carbonate depending on the desired amount of nucleation.

With regard to Claim 79, Doane et al fail to disclose a polymeric protectant layer, moisture protective layer and product contact layer having a thickness of from five to thirty pounds per three thousand feet. However, Doane et al discloses layers comprised in a tray (column 4, lines 10 - 13), as discussed above. It therefore would have been obvious for one of ordinary skill in the art to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package.

## ANSWERS TO APPLICANT'S ARGUMENTS

6. Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 76 – 78 and 80 as being anticipated by Doane et al. (U.S. Patent No. 6,040,063), 35 U.S.C. 103(a) rejection of Claims 74 – 75, 81 – 88 as being unpatentable over Asrar et al (U.S. Patent No. 6,025,028) in view of Lind et al (U.S. Patent 4,267,960) and 35 U.S.C. 103(a) rejection of Claim 79 as being unpatentable over Doane et al. (U.S. Patent No. 6,040,063) of record in the previous Action, have been carefully considered but have not been found to be persuasive for the reasons set forth below.

Applicant argues, on page 7 of the remarks dated June 10, 2011, that although layers '14' and '16' of Doane et al are separate and distinct layers, the layers are not disposed on the interior and exterior surface of the substrate.

However, both layers are clearly disposed on the interior and exterior surfaces of the substrate '12,' as shown in Figure 1.

Applicant also argues on page 7 that Doane et al discloses a tray, but does not disclose a cup.

However, as stated on page 2 of the previous Action, the tray disclosed by Doane et al is in the form of a cup as shown in Figure 1.

Applicant also argues, on page 8, that the calcium carbonate disclosed by Doane et al is a nucleating agent, instead of a filler.

However, as stated on page 5 of the previous Action, because Doane et al discloses calcium carbonate, it is unclear why the calcium carbonate disclosed by Doane et al would fail to provide the properties provided by the claimed calcium carbonate.

Applicant also argues, on page 12, that the previous Action does not explain how the heat - sealable coating of Asrar et al is disposed on the interior surface.

However, because Asrar et al discloses heat sealing of a bag with the coating, Asrar et al discloses a bag having the coating between surfaces that are heat - sealed, therefore on an interior surface. Asrar et al also does not disclose a coating that is disposed on an exterior surface.

Applicant also argues on page 12, that a cup is not disclosed by Lind et al.

However, Applicant has not addressed Figure 1 of Lind et al which discloses a bag in the form of a cup.

Applicant also argues on page 12 that no motivation is provided for the combination of Asrar et al with Lind et al.

However, as stated above, it would have been obvious for one of ordinary skill in the art to provide for the cup – shaped bag in Lind et al in Asrar et al in order to obtain a packaging for meat as taught by Lind et al.

Applicant also argues, on page 14, that the statement in the previous Action that it would have been obvious for one of ordinary skill in the art to vary the weight of the coating of Asrar et al depending on the desired weight of the cup is factually unsupported.

However, because the coating would be a component of the cup, the weight of the cup would clearly be impacted by variance in the thickness of the coating.

Applicant also argues, on page 15, that the calcium carbonate disclosed by Asrar et al is a nucleating agent, instead of a filler.

However, as stated on page 5 of the previous Action, because Asrar et al discloses calcium carbonate, it is unclear why the calcium carbonate disclosed by Asrar et al would fail to provide the properties provided by the claimed calcium carbonate.

Applicant also argues, on page 18, that the statement in the previous Action that it would have been obvious for one of ordinary skill in the art to vary the weight of the coating of Doane depending on the desired weight of the cup is factually unsupported.

However, because the coating would be a component of the cup, the weight of the cup would clearly be impacted by variance in the thickness of the coating.

7. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

8. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497. The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Rena Dye can be reached on 571-272-1498. 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).

/Marc A Patterson/
Primary Examiner, Art Unit 1782

Docket No.: FDS-029388-US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

| | | |
|---|---|---|
| CLEVELAND, et al. | : | GROUP ART UNIT: 1782 |
| SERIAL NO: 11/348,150 | : | EXAMINER: PATTERSON, MARC A. |
| FILED: February 06, 2006 | : | CONFIRMATION #: 5681 |

FOR: BIODEGRADABLE PAPER-BASED LAMINATE WITH OXYGEN AND MOISTURE BARRIER PROPERTIES AND METHOD FOR MAKING BIODEGRADABLE PAPER-BASED LAMINATE

**REQUEST FOR RECONSIDERATION**

United States Patent and Trademark Office
**Customer Service Window, Mail Stop AF**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In response to the Office Action (made FINAL) mailed July 20, 2011, the period for response which is set to expire October 20, 2011, please reconsider the above-captioned application in view of the following remarks. Applicants submit there are good and sufficient reasons, in accordance with 37 CFR § 1.116(b), for entering these remarks. In particular, it is believed these remarks will put the above-captioned application in better condition for appeal.

Applicants respectfully request prompt issuance of an Advisory Action by the Examiner, as the present request for reconsideration is being timely filed on or before two months of the mailing date of the Final Action (*i.e.*, on or before September 20, 2011). See MPEP § 706.07(f). Applicants' representative, Matt M. Eslami, also respectfully requests a telephone conference in the event the Examiner has any questions, comments or suggestions that would place any pending claim not in allowable form in better condition for allowance. Applicant's representative may be reached directly at 513-248-6193.

**The Listing of the Claims** begins on page **2** of this paper.

**Remarks/Arguments** begin on page **5** of this paper.

**IN THE CLAIMS**

The listing of claims will replace all prior versions, and listings, of claims in the application:

**Listing of Claims:**

Claims 1-73. (Canceled).

74. (Previously Presented) A product in the form of a cup comprising a laminate forming a moisture barrier, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface; and

a moisture protectant layer disposed solely on said interior surface of said substrate and comprising at least one biodegradable polyester polymer.

75. (Previously Presented) The product laminate according to claim 74, wherein the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

76. (Previously Presented) A product in the form of a cup comprising a laminate forming moisture barriers, said laminate comprising:

a substrate having a separate interior product contacting surface and a separate exterior surface;

a first moisture barrier layer disposed on said interior surface of said substrate; and

a second moisture protectant layer disposed on said exterior surface of said substrate and comprising at least one biodegradable polyester polymer, wherein the second moisture barrier layer is separate from the first moisture barrier layer disposed on said interior surface of said substrate.

77. (Previously Presented) The product according to Claim 88, wherein the second moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler.

78. (Previously Presented) The product according to Claim 77, wherein the second moisture

protectant layer comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

79. (Previously Presented) The product according to claim 76, wherein the second moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$.

80. (Currently Amended) The product according to Claim 76, wherein the second moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate and starch.

81. (Currently Amended) The product according to Claim 87, wherein the moisture protectant layer further comprises from 5 to 20 percent by weight of at least one filler.

82. (Currently Amended) The product according to 81, wherein the moisture protectant layer comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth.

83. (Previously Presented) The product according to Claim 74, wherein the moisture protectant layer further comprises from 5 to 20 percent by weight of at least one member selected from the group consisting of calcium carbonate and starch.

84. (Previously Presented) The product according to Claim 74, wherein the substrate comprises paperboard; and the moisture protectant layer has a coat weight of from 5 to 30 lbs/3000 $ft^2$ and comprises polylactic acid and from 5 to 20 percent by weight of at least one member selected from the group consisting of calcium carbonate and starch.

85-86 (Cancelled).

87. (Previously Presented) The product according to claim 74, wherein the at least one biodegradable polyester polymer is selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

88. (Previously Presented) The product according to claim 76, wherein the second moisture protectant layer comprises at least one biodegradable polyester polymer selected from the group consisting of compostable polylactic acid and a compostable polyhydroxyalkanoate.

**REMARKS/ARGUMENTS**

**A. Status of Claims**

Favorable reconsideration of this application is respectfully requested. Claims 1-73 and 85-86 have previously been cancelled. Claims 74-84 and 87-88 are currently pending.

**B. Response to Rejection of Claim 76 under 35 U.S.C. § 102(b) as Being Anticipated by Doane**

At page 2 of the Final Office Action ("Final Action"), Claim 76 has again been rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Pat. No. 6,040,063 to Doane et al. (hereafter referred to as (hereafter referred to as "**Doane**"). **This rejection is respectfully traversed with respect to Claim 76**, as currently presented, for at least the following reasons.

In support of the rejection of Claim 76 as being anticipated by **Doane**, the Final Action makes the following allegation:

> ***Allegation 1***: [**Doane**] discloses a laminate comprising [a] substrate (column 4, lines 32-39) and **an interior and exterior moisture protective layer** (coating '16' in Figure 2; column 4, lines 29-31) comprising [a] biodegradable polyester (column 4, line 52).[1]

What Allegation 1 asserts does not support the rejection of Claim 76 as anticipated by **Doane**. Claim 76 is distinguishable over **Doane** in reciting that the second moisture barrier layer of the laminate of the cup, which is disposed on the exterior substrate surface, **is separate from the first moisture barrier layer disposed on the interior substrate surface**. In other words, Claim 76 recites **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate**. By contrast, and contrary to what Allegation 1 asserts, coating layer 16 of **Doane** forms only **one continuous and surrounding exterior layer** with respect structure 12. In fact, and contrary to the requirements of 37 CFR § 1.104(c)(2)[2] and MPEP § 707.05,[3] Allegation 1 provides a

[1] See page 2 of the Final Action (emphasis added).
[2] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

**completely inadequate explanation** as to how **Doane** teaches **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according to amended Claim 76.

In response to Applicants' argument at pages 6-7 of their prior June 10, 2011 Response that **Doane** does not disclose two separate and distinct moisture barrier layers, one each disposed on the interior and exterior surface of the substrate, the Final Action makes the following additional allegation:

> ***Allegation 2***: However, **both layers [i.e., layers 14 and 16] are clearly disposed on the interior and exterior surfaces of the substrate '12'** as shown in Figure 1 [of **Doane**].[4]

What Allegation 2 asserts also does not support the rejection of Claim 76 as anticipated by **Doane**. Applicants agree that layers 14 and 16 shown in FIG. 2 of **Doane** are separate and distinct layers. But, again, and contrary to the requirements of 37 CFR § 1.104(c)(2)[5] and MPEP § 707.05,[6] what Allegation 2 neglects to address, and what is not shown by layers 14 and 16 in FIG. 2 of **Doane**, are one of each of these separate and distinct moisture barrier layers **being disposed on the interior and exterior surface of the substrate** as recited in Claim 76. Instead, layer 14 is disposed on interior layer 12 (which Allegation 2 also **mischaracterizes** as the "substrate"), while layer 16 is disposed on layer 14 (not interior layer 12). Like Allegation 1, Allegation 2 again **mischaracterizes** what is fairly taught by FIG. 2 of **Doane** with respect to the positioning of moisture barrier layers with respect to the interior and exterior surfaces of the substrate according to Claim 76.

If the Examiner still maintains that **Doane** teaches a **cup**[7] comprising a laminate having **two separate** and **distinct moisture barrier layers**, **one each disposed on the**

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[3] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)
[4] See page 5 of the present Office Action (emphasis added).
[5] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)
[6] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)
[7] Page 5 of the Final Action also asserts that page 7 of Applicants' prior June 10, 2011 Response argues that "[**Doane**] is not in the form of a cup." But that assertion **mischaracterizes** what was said at page 7 of Applicants' prior June 10, 2011 Response. Applicants' primary emphasis in their argument at page 7 of their prior June 10, 2011 Response was on **Doane** not teaching a laminate having **two separate** and **distinct moisture barrier layers**, **one each disposed on the interior and exterior surface of the substrate** according

**interior and exterior surface of the substrate** according to Claim 76 based on what is asserted in Allegations 1-2, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 76 under 35 U.S.C. § 102(b) as being anticipated by **Doane** for the same reasons presented in Allegations 1-2, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[8] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claim 76, as currently presented, is patentable over **Doane**. Accordingly, the rejection of this Claim under 35 U.S.C. § 102(b) based on this reference should be withdrawn.

**C. Response to Rejection of Claims 74-75, 81-83, and 87-88 under 35 U.S.C. § 103(a) as Being Unpatentable over Asrar, in view of Lind**

At pages 2-3 of the Final Action, Claims 74, 81-83, and 87-88[9] have again been rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Pat. No. 6,025,028 to Asrar et al (hereafter referred to as "**Asrar**"), in view of U.S. Pat. No. 4,267,960 to Lind et al.

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to Claim 76. In addition, the further assertion at page 5 of the Final Action that the "tray disclosed by" **Doane** "is in the form of a cup as shown in Figure 1" further **mischaracterizes** what even **Doane** identifies element 10 to be (a "foam tray"). See, for example, column 3, lines 56-57. In fact, nowhere does **Doane** even mention that its structure can be a cup according to Claim 76.

[8] See 37 CFR § 1.104(d)(2) which states: "When a rejection in an application is based on facts within the personal knowledge of an employee of the Office, the data shall be as specific as possible, and the reference must be supported, when called for by the applicant, by the affidavit of such employee, and such affidavit shall be subject to contradiction or explanation by the affidavits of the applicant and other persons." Applicants note that in the unpublished case of *In re Sun*, 31 USPQ2d 1451, 1455 (Fed. Cir. 1993), the USPTO argued "the procedures established by 37 C.F.R. Section 1.107(b) (1993) [now 37 CFR § 1.104(d)(2)] ***expressly entitle*** an Applicant, on mere request, to an examiner affidavit that provides [citations that support the Examiner's asserted level of skill in the art]" (emphasis added). Furthermore, in *In re Sun*, the Federal Circuit, held that "this procedure, so readily available, helps save the lack of citation in an office action from possible constitutional infirmity in denying reasonable notice and hence due process." See 31 USPQ2d at 1455. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 18): "If it is not possible for the examiner to provide this type of information, **the examiner might choose instead to provide an affidavit detailing the examiner's own personal knowledge** (as a person approximating one of ordinary skill in the art) of the technology in question (citing 37 CFR § 1.104(d)(2)) (emphasis added)."

[9] As Applicants have even noted in their prior June 10, 2011 Response, Claims 85 and 86 have previously been cancelled, so the reference of this rejection to those Claims is moot.

(hereafter referred to as "**Lind**"). **This rejection is respectfully traversed with respect to these Claims**, as currently presented, for at least the following reasons.

In support of the rejection of Claim 74 as being unpatentable over **Asrar**, in view of **Lind**, the Final Office Action makes the following allegations:

> ***Allegation 3***: [**Asrar**] discloses a laminate comprising a substrate a substrate (paper bag; column 10, lines 59-61) having a heat-sealable coating, **therefore an interior layer**, which is a moisture protective layer comprising [a] biodegradable polyester (column 1, lines 7-11). [**Asrar**] **fails to disclose a substrate in the form of a cup**.[10]
>
> ***Allegation 4***: [**Lind**] **disclose[s] a substrate in the form of a cup** (bag structure shown in Figure 1) for the purpose of obtaining a substrate for packaging meat (column 3, lines 22-23).[11]
>
> ***Allegation 5***: It therefore would have been obvious to one of ordinary skill in the art to provide for a substrate in the form of a cup in order to obtain packaging for a meat as taught by [**Lind**].[12]

What Allegations 3-5 assert does not support the rejection of Claim 74 as unpatentable over **Asrar**, even in view of **Lind**. Claim 74 recites a **product in the form of a cup comprising** the laminate forming a moisture barrier, **said laminate** comprising a substrate having a separate interior product contacting surface and a separate exterior surface, wherein the moisture protectant layer is disposed solely on the interior surface of the substrate. Claim 74 is therefore distinguishable over the teachings of **Asrar** at least with respect to the following features: (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**; (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate.

Contrary to what Allegation 3 asserts, **Asrar** does not teach that its coating (1) is on the interior surface of the substrate when in the form of a cup, and especially (2) is solely on the interior surface of the substrate. Instead, all that **Asrar** says in column 10, lines 59-61, relied upon by Allegation 3 is that the "[p]referred objects suitable for coating" include "cups, paper, paper waste bags, etc." Nothing described in column 10, lines 59-61, of **Asrar** relied upon by Allegation 3 (or in any other portion of **Asrar**) can be construed as teaching

[10] See page 3 of the Final Action (emphasis added).
[11] See page 3 of the Final Action (emphasis added).
[12] See page 3 of the Final Action (emphasis added).

features (1) or (2) of the cup recited in Claim 74. Instead, and contrary to the requirements of 37 CFR § 1.104(c)(2)[13] and MPEP § 707.05,[14] Allegation 3 **never properly explains** how the "heat-sealable coating" of **Asrar** can be considered to be disposed on the interior surface according to Claim 74.

What Allegation 4 asserts again **mischaracterizes** what is fairly taught by **Lind**. Contrary to what Allegation 4 asserts, **Lind** does not teach a substrate in the form of a cup. Instead, as the portions (column 3, lines 22-23 ) of this reference relied upon by Allegation 4 clearly say, **Lind** teaches a "heat sealable meat packaging bag." In fact, and contrary to the requirements of 37 CFR § 1.104(c)(2)[15] and MPEP § 707.05,[16] the basis in Allegation 4 for construing the "meat packaging bag" of **Lind** to be equivalent to the "cup" of Claim 74 is **never explained** and **completely absent** from the Final Action.

Indeed, the basis asserted in Allegation 5 for combining **Lind** with **Asrar** is simply a "conclusory statement" that provides no "rational" explanation for why one of ordinary skill in the art would combine **Lind** with **Asrar** with respect to Claim 74. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[17] In fact, even if **Lind** were combined with **Asrar**, Allegation 5 does not explain how **Lind** supplies features (1) and (2) of Claim 74 which Applicants have asserted above in response to Allegation 3 to be missing from **Asrar**.

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[13] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[14] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

[15] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

[16] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)

17 *See e.g., In re Kahn,* 78 U.S.P.Q.2d 1329, 1336 (Fed. Cir. 2006)(emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id.* See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

If the Examiner still maintains that **Asrar**, in view of **Lind**, teaches (1) a cup comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**, (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate according to amended Claim 74 based on what is asserted in Allegations 3-5, then Applicants assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 74 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, in view of **Lind**, for the same reasons presented in Allegations 3-5, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[18] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

In response to Applicants' argument at pages 11-12 of their prior June 10, 2011 Response that Allegation 3[19] "never properly explains how the 'heat-sealable coating' of **Asrar** can be considered to be disposed on the interior surface according to Claim 74," the Final Action makes the following additional allegation:

> ***Allegation 6***: However, because [**Asrar**] discloses **heat sealing of a bag with the coating**, [**Asrar**] discloses **a bag having the coating between surfaces that are heat-sealed, therefore on an interior surface**. [**Asrar**] also **does not disclose a coating that is disposed on an exterior surface**.[20]

What Allegation 6 asserts also does not support the rejection of Claim 74 as unpatentable over **Asrar**, even in view of **Lind**. Like the response above to Allegation 3, and contrary to what Allegation 6 asserts, **Asrar** does not teach that its coating (1) is on the interior surface of the substrate when in the form of a cup, and especially (2) is solely on the interior surface of the substrate. Instead, and also contrary to the requirements of 37 CFR § 1.104(c)(2)[21] and

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[18] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.
[19] Referred to as "Allegation 5" in the Applicants' prior June 10, 2011 Response.
[20] See page 5 of the Final Action (emphasis added).
[21] 37 CFR § 1.104(c)(2) states, in relevant part, that: "The pertinence of each reference, **if not apparent**, must be clearly explained and each rejected claim specified." (Emphasis added.)

MPEP § 707.05,[22] Allegation 6 (like Allegation 3) **never properly explains** how the "heat-sealable coating" of **Asrar** can be considered to be disposed on the interior surface according to Claim 74.

If the Examiner still maintains that **Asrar**, in view of **Lind**, teaches (1) a cup[23] comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**, (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate according to amended Claim 74 based on what is asserted in Allegations 3-6, then Applicants assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 74 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, in view of **Lind**, for the same reasons presented in Allegations 3-6, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[24] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

In response to Applicants' argument at page 12 of their prior June 10, 2011 Response that Allegation 4[25] that "**Lind** does not teach a substrate in the form of a cup," the Final Action makes the following additional allegation:

> ***Allegation 7***: However, Applicant[s] has not addressed Figure 1 of [**Lind**] which discloses **a bag in the form of a cup**.[26]

What Allegation 7 asserts also does not support the rejection of Claim 74 as unpatentable over **Asrar**, even in view of **Lind**. Like Allegation 4 above, what Allegation 7 asserts **mischaracterizes** what is fairly taught by **Lind** because this reference teaches a bag, not a cup according to Claim 74.

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[22] MPEP § 707.05 (Citation of References) states, in relevant part, that: "When such prior art is cited, its **pertinence should be explained**." (Emphasis added.)
[23] The assertion in Allegation 7 that "Applicant[s have] not addressed Figure 1 of [**Lind**] which discloses a bag in the form of a cup" at page 12 of their prior June 10, 2011 Response **is nonsensical**. Figure 1 shows a bag, **not a cup**, no matter what Allegation 7 asserts [**Lind**] teaches.
[24] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.
[25] Referred to as "Allegation 6" in the Applicants' prior June 10, 2011 Response.
[26] See page 5 of the Final Action (emphasis added).

In response to Applicants' argument at page 12 of their prior June 10, 2011 Response that Allegation 5[27] "is simply a "conclusory statement" that provides no 'rational' explanation for why one of ordinary skill in the art would combine **Lind** with **Asrar** with respect to Claim 74," the Final Action makes the following additional allegation:

> ***Allegation 8***: However, as stated above, it would have been obvious for one of ordinary skill in the art to provide for the cup-shaped bag in [**Lind**] in [**Asrar**] in order to obtain a packaging for meat as taught by [**Lind**].[28]

What Allegation 8 asserts also does not support the rejection of Claim 74 as unpatentable over **Asrar**, even in view of **Lind**. Like the response above to Allegation 5, the basis asserted in Allegation 8 for combining **Lind** with **Asrar** is simply a "conclusory statement" that provides no "rational" explanation for why one of ordinary skill in the art would combine **Lind** with **Asrar** with respect to Claim 74. Also, even if **Lind** were combined with **Asrar**, Allegation 8 still does not explain how **Lind** supplies features (1) and (2) of Claim 74 which Applicants have asserted above in response to Allegation 3 to be missing from **Asrar**.

If the Examiner still maintains that **Asrar**, in view of **Lind**, teaches (1) a **cup**[29] comprising a laminate having **a moisture protectant layer disposed on the interior surface of the substrate**, (2) wherein the moisture protectant layer is disposed **solely** on the interior surface of the substrate according to amended Claim 74 based on what is asserted in Allegations 7-8, then Applicants again assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 74 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, in view of **Lind**, for the same reasons presented in Allegations 7-8, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[30] because this rejection appears to be based, at least partially, on facts within the Examiner's

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[27] Referred to as "Allegation 7" in the Applicants' prior June 10, 2011 Response.
[28] See page 6 of the Final Action (emphasis added).
[29] The assertion in Allegation 7 that "Applicant[s have] not addressed Figure 1 of [**Lind**] which discloses a bag in the form of a cup" at page 12 of their prior June 10, 2011 Response **is nonsensical**. Figure 1 shows a bag, **not a cup** according to Claim 74, no matter what Allegation 7 asserts, as well as **mischaracterizes** [**Lind**] to teach.
[30] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.

personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 75 and 84 as being unpatentable over **Asrar**, in view of **Lind**, the present Office Action makes the following allegations:

> ***Allegation 9***: [**Asrar**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Asrar**] discloses layers comprised in a cup, as discussed above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[31]

What Allegation 9 asserts again does not support the rejection of Claims 75 or 84 as being unpatentable over **Asrar**, for at least the following reasons. First, for at least the same reasons presented above in response to Allegations 3-6, Claim 74 is patentable over **Asrar**. Allegation 9 does not assert that those features of Claim 74 (i.e., a cup comprising a laminate having a moisture barrier layer **which is disposed solely on the interior product contacting surface**) which were asserted **to be missing from the teachings** of **Asrar** are now taught by that reference. Claims 75 and 84 also depend directly from Claim 74, and are therefore patentable over **Asrar** (even in view of **Lind**) for at least the same reasons presented above in response to Allegations 3-6 for why Claim 74 is patentable over this reference.

Second, Allegation 9 concedes that the coat weights (not **thickness** as asserted in Allegation 8) recited in amended Claims 75 and 84 are not taught by **Asrar**. Instead, Allegation 8 asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually supported** by **Asrar**, the reference primarily relied upon in rejecting Claims 75 and 84. "Rejections on obviousness grounds cannot be sustained by mere **conclusory statements**; instead there must

[31] See page 3 of the present Office Action (emphasis added).

be some **articulated reasoning** with some **rational underpinning** to support the legal conclusion of obviousness."[32]

In response to Applicants' argument at page 14 of their prior June 10, 2011 Response that Allegation 9[33] "is simply a "conclusory statement" that provides no 'rational' explanation for why one of ordinary skill in the art would combine **Lind** with **Asrar** with respect to Claim 74," the Final Action makes the following additional allegation:

> ***Allegation 10***: However, because the coating would be a component of the cup, **the weight of the cup would clearly be impacted by variance in the thickness**.[34]

Like Allegation 9, what Allegation 10 asserts also does not support the rejection of Claims 75 and 84 as unpatentable over **Asrar**, even in view of **Lind**. First, like Allegation 9, what Allegation 10 asserts is still an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually supported** by **Asrar**, the reference primarily relied upon in rejecting Claims 75 and 84. In asserting that "the weight of the cup would clearly be impacted by variance in the thickness," Allegation 10 makes a **clear admission of speculation by the Examiner having no factual support** in the references relied upon (i.e., **Asrar**). In fact, in view of what Allegations 9 and 10 assert, it again appears that the Examiner is rejecting Claims 75 and 84 as being unpatentable over **Asrar**, even in view of **Lind**, based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claims 75 and 84 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, even in view of **Lind**, for the same reasons presented in Allegations 9 and 10, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR

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[32] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id.* See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

[33] Referred to as "Allegation 8" in the Applicants' prior June 10, 2011 Response.

[34] See page 6 of the Final Action (emphasis added).

§ 1.104(d)(2)[35] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, **Lind**, or any other verifiable evidence provided by the Examiner.

In support of the rejection of Claims 81-83, and 87-88 as being as being unpatentable over **Asrar**, in view of **Lind**, the present Office Action makes the following allegation:

> ***Allegation 11***: [**Asrar**] discloses [a] polyester comprising polyhydroxyalkanoate (column 10, line[s] 54-55) and a **filler** comprising calcium carbonate (column 8, lines 59-60).[36]

What Allegation 11 asserts also does not support the rejection of amended Claims 81-83 and Claims 87-88 as being unpatentable over **Asrar**, even in view of **Lind**. Amended Claims 81-83 and Claim 87 depend, directly or indirectly, from Claim 74. Accordingly, amended Claims 81-83 and Claim 87 are patentable over **Asrar** for at least the same reasons presented above in response to Allegations 3-5 for why Claim 74 is patentable over this reference, even in view of what **Lind** teaches.

In addition, amended Claims 81-83 are further distinguishable over **Asrar**, even in view of **Lind**, in reciting that the moisture protectant layer comprises **at least one filler** which may be calcium carbonate (see amended Claim 82). First, Allegation 11 has **mischaracterized** what is fairly taught by **Asrar** with regard to the use of calcium carbonate. Contrary to what Allegation 11 asserts, **Asrar** does not teach that calcium carbonate is being used as a filler according to amended Claims 81-83. Instead, **Asrar** teaches inorganic compounds such as metal oxides, metal hydroxides, and metal carbonates, preferably of metals such as aluminum, antimony, tin, sodium, calcium, magnesium, barium or zinc, "can be used to further improve nucleation activity and/or reduce the extent of discoloration and/or improve the clarity of PHA-derived products when used in combination" with ODPA nucleants to form **Asrar's** coating comprising the PHAs.[37] Nothing in **Asrar** suggests that calcium carbonate is being used as a filler according to amended Claims 81-83.[38]

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[35] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.
[36] See page 3 of the present Office Action (emphasis added).
[37] See column 8, lines 53-63, of **Asrar**.
[38] Page 6 of the Final Action responds by asserting that "it is unclear why the calcium carbonate disclosed by [**Asrar**] would fail to provide the properties provided by the claimed carbonate." But the purpose that **Asrar**

In further response to what Allegation 11 erroneously asserts, Claims 81-83 recite that the "at least one filler" (e.g., calcium carbonate) comprises **from 5 to 20 percent by weight** of the respective moisture protectant layer. **Asrar** teaches that its "metal oxides, metal hydroxides, and metal carbonates" may be used with the ODPA nucleants in an amount of from 0.001 to 5 parts (most preferably from about 0.01 to 0.5 parts) per hundred parts of the PHA resin.[39] But **Asrar** also teaches that the ODPA nucleants may be used in an amount of from 0.01 to 5 parts (most preferably from about 0.02-0.5 parts) per hundred parts of the PHA resin.[40] Accordingly, given that **Asrar** does not teach what amounts of these "metal carbonates" should be used with what amounts of these ODPA nucleants, one of ordinary skill in this art would have no basis from this reference for selecting the amounts of "filler" recited in amended Claims 81-83.

If the Examiner still maintains that **Asrar** teaches **at least one filler** in the moisture protectant layer **in an amount of from 5 to 20 percent weight** according to amended Claims 81-83 based on what is asserted in Allegation 11, then Applicants also assert that this rejection under 35 U.S.C. § 102(b) appears to be based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of amended Claims 81-83 under 35 U.S.C. § 103(a) as being unpatentable over **Asrar**, even in view of **Lind**, for the same reasons presented in Allegation 11, Applicants **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[41] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Asrar**, **Lind**, or any other verifiable evidence provided by the Examiner.

For at least the foregoing reasons, Claims 74-7, 81-84, and 87-88, as currently presented, are patentable over **Asrar**, even in view of **Lind**. Accordingly, the rejection of these Claims under 35 U.S.C. § 103(a) over this combination of references should be withdrawn.

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teaches for including calcium carbonate is clearly relevant, particularly with respect to whether this reference teaches the amounts recited in Claims 81-83 for the calcium carbonate used as filler. See argument in paragraph following.

[39] See column 9, lines 1-8, of **Asrar**.

[40] See column 8, lines 43-45, of **Asrar**.

[41] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.

**D. Response to Rejection of Claims 77-80 under 35 U.S.C. § 103(a) as Being Unpatentable over Doane**

At page 3 of the Final Action, Claims 77-80 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over **Doane**. **This rejection is respectfully traversed with respect to these Claims**, as currently presented, for at least the following reasons.

In support of the rejection of Claims 77-78 under 35 U.S.C. § 103(a) as being unpatentable over **Doane**, the Final Action makes the following allegation:

> ***Allegation 12***: [**Doane**] fails to disclose a calcium carbonate in the amount of 5-20% by weight. However, the calcium carbonate disclosed by [] is for nucleation (column 9, lines 38-41). It there would have been obvious for one of ordinary skill in the art to select an amount of calcium carbonate depending on the desired amount.[42]

What Allegation 12 asserts does not support the rejection of Claims 77-78 as being unpatentable over **Doane** for at least the following reasons. First, for at least the same reasons presented above in Section B in response to Allegations 1-2, Claim 76 is patentable over **Doane**. Allegation 12 does not assert that those features recited in Claim 77 (i.e., second moisture barrier layer comprising from 5 to 20 percent by weight of at least one filler) or recited in Claim 78 (i.e., second moisture protectant layer comprises from 5 to 20 percent by weight of at least one filler selected from the group consisting of calcium carbonate, starch, clay kaolin, talc, cellulose fibers, and diatomaceous earth) which were asserted **to be missing from the teachings** of **Doane** are now taught by that reference.[43]

In support of the rejection of Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane**, the Final Action makes the following allegation:

> ***Allegation 13***: [**Doane**] **fails to disclose** a polymeric protectant layer, moisture protective layer and product contact layer having a **thickness** of from five to thirty pounds per three thousand feet. However, [**Doane**] discloses layers comprised in a tray (column 4, lines 10-13), as discussed

[42] See page 4 of the Final Action (emphasis added).
[43] Similar to the assertion made at page 6 of the Final Action with respect to what **Asrar** teaches with respect to the calcium carbonate filler of Claims 81-83, page 5 of the Final Action also asserts "it is unclear why the calcium carbonate disclosed by [**Doane**] would fail to provide the properties provided by the claimed carbonate [of Claims 77-78 and 80]." But, again, the purpose that **Doane** teaches for including calcium carbonate is clearly relevant, particularly with respect to whether this reference teaches the amounts recited in Claims 77-78 and 80 for the calcium carbonate used as filler.

> above. **It therefore would have been obvious** for one of ordinary skill in the art **to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package**.[44]

What Allegation 13 asserts again does not support the rejection of Claim 79 as being unpatentable over **Doane** for at least the following reasons. First, for at least the same reasons presented above in Section B in response to Allegations 1-2, Claim 76 is patentable over **Doane**. Allegation 13 does not assert that those features in Claim 76 (i.e., the second moisture barrier layer disposed on the exterior substrate surface **is separate from the first moisture barrier layer disposed on the interior substrate surface**) which were asserted **to be missing from the teachings** of **Doane** are now taught by that reference. Claim 79 also depends directly from Claim 76, and is therefore patentable over **Doane** for at least the same reasons presented above in response to Allegations 1-2 for why Claim 76 is patentable over this reference.

Second, Allegation 13 concedes that the coat weights (not **thickness** as asserted by Allegation 10) recited in amended Claim 79 are not taught by **Doane**. Instead, Allegation 13 asserts that it "would be obvious . . . to have provided for a desired coat weight of polymeric protectant layer, moisture protective layer and product contact layer depending on the desired weight of the package." That assertion again amounts to an **impermissible** "conclusory statement" without any "rational underpinning" which is **factually unsupported** by **Doane**,[45] the reference relied upon in rejecting amended Claim 79.[46]

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[44] See page 4 of the Final Action (emphasis added).

[45] Page 6 of the Final Action further asserts that "because the coating would be a component of the cup, the weight of the cup would clearly be impacted by variance in the thickness of the coating." But that assertion, again, provides **no factually supported basis** in **Doane** for why this reference would teach the **specific coat weights** recited in Claim 79. See also response to Allegation 10 in Section C above.

[46] *See e.g., In re Kahn,* 78 U.S.P.Q.2d at 1336 (emphasis added), cited with approval in the Supreme Court's decision in *KSR International Co. v. Teleflex, Inc*., 550 U.S. 398, 418 (2007). In *KSR International*, the Supreme Court also observed "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." *Id*. See also *In re Vaidyanathan* (Fed. Cir. 2010)(non-precedential)(slip opinion at 17): "Obviousness is determined as a matter of foresight, not hindsight. [Citations to *KSR International* and *Graham v. John Deere Co.* omitted]. *KSR* [*International*] did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, **the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known**. Instead, **the examiner should** elaborate, **discuss**ing **the evidence or reasoning that leads the examiner to such a conclusion** (emphasis added).

Allegation 13 points to **absolutely nothing** in **Doane** (or any other verifiable evidence) to **factually support** why one of ordinary skill in the art would select the particular coat weights recited in Claim 79. In fact, it again appears that the Examiner is rejecting Claim 79 as being unpatentable over **Doane** based, at least partially, on facts within the Examiner's personal knowledge **which have not been provided to Applicants**. Accordingly, if the Examiner wishes to persist in this rejection of Claim 79 under 35 U.S.C. § 103(a) as being unpatentable over **Doane** for the same reasons presented in Allegation 13, Applicants again **respectfully request** that he provide an affidavit/declaration under 37 CFR § 1.104(d)(2)[47] because this rejection appears to be based, at least partially, on facts within the Examiner's personal knowledge which have not been provided to Applicants, and which are not fairly taught or suggested by **Doane**, or any other verifiable evidence provided by the Examiner.

With respect to Claim 80 (which depends directly from Claim 76), and contrary to the requirements of 37 CFR § 1.104(b),[48] provides **absolutely no explanation** as to what the rejection of Claim 80 as being unpatentable over **Doane** is based on. Nonetheless, for at least the same reasons presented above in response to Allegations 12 and 13, Claim 80 is patentable over **Doane**.

For at least the foregoing reasons, Claims 77-80, as currently presented, are patentable over **Doane**. Accordingly, the rejection of these Claims under 35 U.S.C. § 103(a) over this reference should be withdrawn.

## E. Conclusion

Claims 74-84 and 87-88, as currently presented, are patentable over the art relied upon in the Final Action. Accordingly, Claims 74-84 and 87-88 are in condition for allowance, and favorable action is earnestly solicited thereon.

Should the Examiner feel that there are any issues outstanding after consideration of this response, the Examiner is invited to contact the undersigned at 513-248-6193 to expedite prosecution of the above application.

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[47] See footnote regarding what 37 CFR § 1.104(d)(2) states and relevant case law interpreting same.
[48] 37 CFR § 1.104(b) states, in relevant part, that: "The examiner's action **will be complete as to all matter**." (Emphasis added.)

No extension of time is believed to be required. However, the Commissioner is hereby authorized by this paper to charge any fees due under 37 C.F.R. §§ 1.16 and 1.17 which may be required, including any required extension of time fees, or credit any overpayment, to Deposit Account No. 09-0525. **This paragraph is intended to be a CONSTRUCTIVE PETITION FOR EXTENSION OF TIME in accordance with 37 C.F.R. § 1.136(a)(3) if needed.**

Respectfully Submitted,

Date: September 2, 2011

By: /Matthew M. Eslami/

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| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 10870036 |
| **Application Number:** | 11348150 |
| **International Application Number:** | |
| **Confirmation Number:** | 5681 |
| **Title of Invention:** | Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate |
| **First Named Inventor/Applicant Name:** | Christopher S. Cleveland |
| **Customer Number:** | 01726 |
| **Filer:** | Matthew M. Eslami/Michele McRoy |
| **Filer Authorized By:** | Matthew M. Eslami |
| **Attorney Docket Number:** | FDS-029388-US |
| **Receipt Date:** | 02-SEP-2011 |
| **Filing Date:** | 06-FEB-2006 |
| **Time Stamp:** | 11:39:16 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| Submitted with Payment | no |
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## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes)/ Message Digest | Multi Part /.zip | Pages (if appl.) |
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| 1 | | 110902_reqforreconsideration_fds029388us.pdf | 219706<br>0b9ef33076d84d798f8021dae7cebf2e594c136a | yes | 20 |

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| | **Document Description** | **Start** | **End** |
| | Amendment After Final | 1 | 1 |
| | Claims | 2 | 4 |
| | Applicant Arguments/Remarks Made in an Amendment | 5 | 20 |
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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 (07-06)
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# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | ☐ To be Mailed |
|---|---|---|
| 11/348,150 | 02/06/2006 | |

## APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY ☐ RATE ($) | SMALL ENTITY ☐ FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY FEE ($) |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | | | | | |
| ☒ BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | 300 |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | 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 $250 ($125 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 | | | TOTAL | 300 |

## APPLICATION AS AMENDED – PART II

AMENDMENT 09/02/2011

| | (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)) | * 13 | Minus | ** 73 | = 0 | X $ = | | OR | X $52= | 0 |
| Independent (37 CFR 1.16(h)) | * 2 | Minus | ***13 | = 0 | X $ = | | OR | X $220= | 0 |
| ☐ 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 | 0 |

AMENDMENT

| | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| 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 number found in the appropriate box in column 1.

Legal Instrument Examiner:
/FELICIA ALLEN-JENKINS/

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.**

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 09/26/2011

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
LOVELAND, OH 45140

| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 09/26/2011 | PAPER |

**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.

**ADVISORY ACTION**

*Applicant's arguments filed September 2, 2011 have been fully considered but have not been found to be persuasive.*

1. Applicant argues, on page 5 of the remarks dated September 2, 2011, that Doane fails to disclose two separate and distinct moisture barrier layers, one each disposed on the interior and exterior surface of the substrate, because the second moisture barrier layer disclosed by Doane is disposed on the first moisture barrier layer instead of being disposed on the surface of the substrate.

However, because the first moisture barrier layer '14' is disposed on the surface of the substrate, the second moisture barrier layer is also disposed on the surface of the substrate, although it is not in direct contact with the substrate.

Applicant also argues, on page 8, that nothing in Asrar et al teaches that the disclosed heat sealable layer is disposed on the interior surface of the disclosed cup or bag and that the previous Action does not explain.

However, because Asrar et al disclose a heat sealable layer, Asrar et al disclose a bag that is made by heat sealing and having an innermost layer comprising a heat sealing layer. Furthermore, a bag that is made by heat sealing and having an innermost layer comprising a heat sealing layer is taught by Lind et al.

Applicant also argues, on page 9, that Lind et al teach a bag instead of a substrate in the form of a cup and that Lind et al teach a meat packaging bag.

However, although a bag is disclosed by Lind et al, a cup shape is clearly shown in Figure 1 of Lind et al.

Applicant also argues, on page 13, that the statement that the weight of the cup would be impacted by the variance in the thickness is an impermissibly conclusory statement.

However, because the cup and coating are physically bonded, the statement is a permissibly conclusory statement.

Applicant also argues, on page 15, that Asrar et al do not disclose a filler comprising calcium carbonate, because Asrar et al disclose calcium carbonate to improve nucleation and that the claimed amount of 5 to 100 percent by weight is not disclosed by Asrar et al. However, as stated in the previous Action, it would have been obvious for one of ordinary skill in the art to select an amount of calcium carbonate, depending on the desired amount of nucleation, and the selection of an amount between 5 to 100 percent by weight would be expected to produce the same structural properties as a filler.

2. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497. The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Rena Dye can be reached on 571-272-1498. 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).

/Marc A Patterson/
Primary Examiner, Art Unit 1782

| **Advisory Action Before the Filing of an Appeal Brief** | **Application No.** 11/348,150 | **Applicant(s)** CLEVELAND ET AL. | |
|---|---|---|---|
| | **Examiner** MARC PATTERSON | **Art Unit** 1782 | |

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

THE REPLY FILED 02 September 2011 FAILS TO PLACE THIS APPLICATION IN CONDITION FOR ALLOWANCE.

1. ☒ The reply was filed after a final rejection, but prior to or on the same day as filing a Notice of Appeal. To avoid abandonment of this application, applicant must timely file one of the following replies: (1) an amendment, affidavit, or other evidence, which places the application in condition for allowance; (2) a Notice of Appeal (with appeal fee) in compliance with 37 CFR 41.31; or (3) a Request for Continued Examination (RCE) in compliance with 37 CFR 1.114. The reply must be filed within one of the following time periods:
   a) ☐ The period for reply expires _____months from the mailing date of the final rejection.
   b) ☒ The period for reply expires on: (1) the mailing date of this Advisory Action, or (2) the date set forth in the final rejection, whichever is later. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of the final rejection.

   Examiner Note: If box 1 is checked, check either box (a) or (b). ONLY CHECK BOX (b) WHEN THE FIRST REPLY WAS FILED WITHIN TWO MONTHS OF THE FINAL REJECTION. See MPEP 706.07(f).

Extensions of time may be obtained under 37 CFR 1.136(a). The date on which the petition under 37 CFR 1.136(a) and the appropriate extension fee have been filed is the date for purposes of determining the period of extension and the corresponding amount of the fee. The appropriate extension fee under 37 CFR 1.17(a) is calculated from: (1) the expiration date of the shortened statutory period for reply originally set in the final Office action; or (2) as set forth in (b) above, if checked. Any reply received by the Office later than three months after the mailing date of the final rejection, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

NOTICE OF APPEAL

2. ☐ The Notice of Appeal was filed on _____. A brief in compliance with 37 CFR 41.37 must be filed within two months of the date of filing the Notice of Appeal (37 CFR 41.37(a)), or any extension thereof (37 CFR 41.37(e)), to avoid dismissal of the appeal. Since a Notice of Appeal has been filed, any reply must be filed within the time period set forth in 37 CFR 41.37(a).

AMENDMENTS

3. ☐ The proposed amendment(s) filed after a final rejection, but prior to the date of filing a brief, will not be entered because
   (a) ☐ They raise new issues that would require further consideration and/or search (see NOTE below);
   (b) ☐ They raise the issue of new matter (see NOTE below);
   (c) ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal; and/or
   (d) ☐ They present additional claims without canceling a corresponding number of finally rejected claims.

   NOTE: _____. (See 37 CFR 1.116 and 41.33(a)).
4. ☐ The amendments are not in compliance with 37 CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☐ Applicant's reply has overcome the following rejection(s): _____.
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☒ For purposes of appeal, the proposed amendment(s): a) ☐ will not be entered, or b) ☒ will be entered and an explanation of how the new or amended claims would be rejected is provided below or appended.
   The status of the claim(s) is (or will be) as follows:
   Claim(s) allowed: *none*.
   Claim(s) objected to: *none*.
   Claim(s) rejected: *74-84,87 and 88*.
   Claim(s) withdrawn from consideration: *none*.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ The affidavit or other evidence filed after a final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
9. ☐ The affidavit or other evidence filed after the date of filing a Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing a good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
10. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

11. ☐ The request for reconsideration has been considered but does NOT place the application in condition for allowance because: _____.
12. ☐ Note the attached Information *Disclosure Statement*(s). (PTO/SB/08) Paper No(s). _____
13. ☒ Other: See attached.



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
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Docket No.: FDS-029388-US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

| | | |
|---|---|---|
| CLEVELAND, et al. | : | GROUP ART UNIT: 1782 |
| SERIAL NO: 11/348,150 | : | EXAMINER: PATTERSON, MARC A. |
| FILED: February 06, 2006 | : | CONFIRMATION #: 5681 |

FOR: BIODEGRADABLE PAPER-BASED LAMINATE WITH OXYGEN AND MOISTURE BARRIER PROPERTIES AND METHOD FOR MAKING BIODEGRADABLE PAPER-BASED LAMINATE

O.K. to enter

/M.P./

09/22/2011

**REQUEST FOR RECONSIDERATION**

United States Patent and Trademark Office
**Customer Service Window, Mail Stop AF**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In response to the Office Action (made FINAL) mailed July 20, 2011, the period for response which is set to expire October 20, 2011, please reconsider the above-captioned application in view of the following remarks. Applicants submit there are good and sufficient reasons, in accordance with 37 CFR § 1.116(b), for entering these remarks. In particular, it is believed these remarks will put the above-captioned application in better condition for appeal.

Applicants respectfully request prompt issuance of an Advisory Action by the Examiner, as the present request for reconsideration is being timely filed on or before two months of the mailing date of the Final Action (*i.e.*, on or before September 20, 2011). See MPEP § 706.07(f). Applicants' representative, Matt M. Eslami, also respectfully requests a telephone conference in the event the Examiner has any questions, comments or suggestions that would place any pending claim not in allowable form in better condition for allowance. Applicant's representative may be reached directly at 513-248-6193.

**The Listing of the Claims** begins on page **2** of this paper.

**Remarks/Arguments** begin on page **5** of this paper.

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. |
|---|---|---|---|---|
| 11/348,150 | 02/06/2006 | Christopher S. Cleveland | FDS-029388-US | 5681 |

1726 7590 09/30/2011

INTERNATIONAL PAPER COMPANY
6285 TRI-RIDGE BOULEVARD
LOVELAND, OH 45140

| EXAMINER | |
|---|---|
| PATTERSON, MARC A | |
| ART UNIT | PAPER NUMBER |
| 1782 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 09/30/2011 | PAPER |

**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.

| Examiner-Initiated Interview Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 11/348,150 | CLEVELAND ET AL. | |
| | Examiner | Art Unit | |
| | MARC PATTERSON | 1782 | |

All participants (applicant, applicant's representative, PTO personnel):

(1) *Marc Patterson*.

(2) *Matt Eslami (Reg. No. 45,488)*.

(3) *Eric Guttag (Reg. No. 28,853)*.

(4) *Thomas Ryan (Reg, No. 43,072)*.

Date of Interview: *28 September 2011*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☐ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☒103 ☐Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: *all of the record*.

Identification of prior art discussed: *all of the record*.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

*The claimed invention vs the prior art of record, specifically amendments regarding the structure of the claimed invention that may distinguish over the prior art of record*.

**Applicant recordation instructions**: It is not necessary for applicant to provide a separate record of the substance of interview.

**Examiner recordation instructions**: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

| /Marc A Patterson/<br>Primary Examiner, Art Unit 1782 | |
|---|---|



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
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Doc code: RCEX
Doc description: Request for Continued Examination (RCE)

PTO/SB/30EFS (07-09)
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.

# REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
## (Submitted Only via EFS-Web)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Application Number | 11/348,150 | Filing Date | 2006-02-06 | Docket Number (if applicable) | FDS-029388-US | Art Unit | 1782 |
| First Named Inventor | Christopher S. Cleveland | | | Examiner Name | Patterson, Marc A. | | |

**This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.**
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

### SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

- ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
- ☐ Other _____

☒ Enclosed

- ☒ Amendment/Reply
- ☐ Information Disclosure Statement (IDS)
- ☐ Affidavit(s)/ Declaration(s)
- ☐ Other _____

### MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____
(Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

### FEES

**The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**

☒ The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 090525

### SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

☐ Applicant Signature

PTO/SB/30EFS (07-09)
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.

| Signature of Registered U.S. Patent Practitioner | | | |
|---|---|---|---|
| Signature | /Matthew M. Eslami/ | Date (YYYY-MM-DD) | 2011-10-10 |
| Name | Matthew M. Eslami | Registration Number | 45488 |

This collection of information is required by 37 CFR 1.114. 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.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

## 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 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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PTO/SB/08a (01-10)
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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 | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

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| Examiner Initial* | Cite No | Foreign Document Number[3] | Country Code[2] i | 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 | 2150377 | CA | | 1994-04-28 | Suskind | | ☐ |
| | 2 | 2179522 | CA | | 1995-06-29 | Waddington | | ☐ |
| | 3 | 11128284 | JP | | 1999-05-18 | Nakamura et al. | | ☒ |

| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
|---|---|---|
| | Application Number | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 4 | 199631347 | WO | | 1996-10-10 | Waddington | | ☐ |
| | 5 | 200160143 | WO | | 2001-08-23 | Lee et al. | | ☐ |
| | 6 | 2003128898 | JP | | 2003-05-08 | Kunihiro et al. | | ☒ |
| | 7 | 2003220668 | JP | | 2003-08-05 | Takashi | | ☒ |

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

**NON-PATENT LITERATURE DOCUMENTS** Remove

| 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 | Ewa Rudnik, "Compostable Polymer Materials", 1st Ed., Page 43, 2008 | ☐ |
| | 2 | Michael and Irene Ash, "Handbook of Green Chemicals", 2nd Ed., Page 564, 2004 | ☐ |

If you wish to add additional non-patent literature document citation information please click the Add button Add

**EXAMINER SIGNATURE**

| Examiner Signature | | Date Considered | |
|---|---|---|---|

*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.

EFS Web 2.1.17

| INFORMATION DISCLOSURE STATEMENT BY APPLICANT ( Not for submission under 37 CFR 1.99) | | |
|---|---|---|
| | Application Number | 11348150 |
| | Filing Date | 2006-02-06 |
| | First Named Inventor | CLEVELAND, CS |
| | Art Unit | 1782 |
| | Examiner Name | Patterson, Marc A. |
| | Attorney Docket Number | FDS-029388-US |

**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 | /Matthew M. Eslami/ | Date (YYYY-MM-DD) | 2011-10-10 |
|---|---|---|---|
| Name/Print | Matthew M. Eslami | Registration Number | 45488 |

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.**

## Privacy Act Statement

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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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Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2150377 C 2002/04/30

(11)(21) 2 150 377

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 1993/10/15
(87) Date publication PCT/PCT Publication Date: 1994/04/28
(45) Date de délivrance/Issue Date: 2002/04/30
(85) Entrée phase nationale/National Entry: 1995/05/26
(86) N° demande PCT/PCT Application No.: US 1993/009686
(87) N° publication PCT/PCT Publication No.: 1994/009210
(30) Priorité/Priority: 1992/10/16 (07/962,100) US

(51) Cl.Int.$^{6}$/Int.Cl.$^{6}$ D21H 19/28, B65D 65/46, D21H 27/36
(72) Inventeur/Inventor:
Suskind, Stuart P., US
(73) Propriétaire/Owner:
Pearlstein, Leonard, US
(74) Agent: SMART & BIGGAR

(54) Titre : EMBALLAGE COMPOSTABLE POUR LIQUIDES
(54) Title: COMPOSTABLE PACKAGING FOR CONTAINMENT OF LIQUIDS

(57) Abrégé/Abstract:
A compostable paperboard container and package for liquids which is coated with a material capable of degrading to carbon dioxide, water and biomass under composting conditions.



Clearwater Paper Corp. - EX1002
Clearwater Paper Corp. v. Graphic Packaging International LLC
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**PCT** WORLD INTELLECTUAL PROPERTY ORGANIZATION
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: COMPOSTABLE PACKAGING FOR CONTAINMENT OF LIQUIDS

(57) Abstract

A compostable paperboard container and package for liquids which is coated with a material capable of degrading to carbon dioxide, water and biomass under composting conditions.

Description

COMPOSTABLE PACKAGING FOR CONTAINMENT OF LIQUIDS

Technical Field

The present invention relates to a compostable container for containing liquids or liquid containing materials. The present invention furthers relates to a paperboard container having a degradable coating on at least one of the internal or external surfaces thereof. More particularly, the present invention relates to a paperboard container which will biodegrade to carbon dioxide, water and biomass under composting conditions. The present invention further relates to a method of making and a method of using the degradable container.

Background Art

In the management of Municipal Solid Waste (MSW), the expectation that paper and paper products would biodegrade in landfills has proven to be unreliable. In fact, newspapers buried for over fifty year have been recovered from landfills in readable condition. Since paper comprises about 50% of landfill space, it has become an important priority to find alternate ways to manage paper waste.

Recycling paper, often with the removal of printing inks and coatings, has proven to be economically feasible when the recovered pulp fibers find new markets and applications. Fiber recovery, and, in particular, repeated fiber recoveries tend to damage, break, and otherwise reduce the quality of paper fiber. This degradation in paper quality often results in a product with limited or nonexistent new markets or applications.

Since paper has the inherent property of biodegradability under appropriate conditions, more attractive alternates to simple landfilling have received increased attention. Among these, is the process of composting, in which waste is degraded to humus or biomass under accelerated and controlled conditions of moisture, air and microorganisms. More specifically, paper, under

composting conditions is converted into carbon dioxide, water, and biomass. The biomass is essentially comprised of microorganisms. Thus, the mass of waste is significantly reduced and the humus by-product has commercial value as low grade fertilizer, soil conditioner, and as a mulch for land and agricultural applications.

Paper products are often coated with resins or plastic materials to provide barrier properties when they will be used in the containment of liquids. The most important requirements for these structures when intended for use as folded cartons to contain liquid products include:

a. barrier properties to reduce and prevent absorption and/or transmission of liquid components;

b. heat sealability for carton construction and integrity;

c. printability to provide attractive, non-functional graphics;

d. vapor barriers to contain fragrances, flavors, moisture, etc.;

e. barriers to oxygen and other ambient gases;

f. rigidity, shape retention, and crush resistance.

Typical constructions of important commercial value include milk cartons in which the paperboard coating composition is low density polyethylene; fruit juice containers as described in U.S. Reissue Patent No. 33,376; and wet wipe container.

Such constructions meet the requirements stated above in (a)-(f), however, such constructions are compostable only to the degree to which cellulose pulp is present, typically around

85%. Under composting conditions, the pulp fibers would be expected to decompose leaving a residue of biologically inert plastic.

## Disclosure of the Invention

It is therefore an object of the invention to overcome these and other difficulties encountered in the prior art.

Given the current waste disposal problems, another object of the present invention is to provide a container for liquids which meets requirements (a)-(f) and which will also degrade to carbon dioxide, water and biomass under composting conditions.

Another object of the present invention is to provide liquid barrier properties to pulp based substrates which are degradable under composting conditions by coating with polymers selected from the group of aliphatic polyesters.

A further object of the invention is to provide, as an environmentally improved alternate to plastic, a completely degradable packaging material for the containment of liquids and wet products.

Still another object of the invention is to provide crush-resistant, durable packaging material suitable for liquids and wet products.

A further object of the invention is to provide coated packaging material for use in folded cartons in which the coating has a composting rate approximately equal to the pulp based substrate.

Another object of the invention is to provide special properties to coatings of biodegradable aliphatic polyesters, by blending to about 30% by weight with polymers or fillers that are either miscible or mechanically compatible.

To achieve the objects and in accordance with the purpose of the invention, as embodied and broadly described herein, the invention comprises a compostable package for containing liquids or wet products including a base of paperboard having coated thereon a polymeric material capable of preventing leaks wherein said base and said polymeric material degrades to form carbon dioxide, water and biomass.

In another aspect of the invention there is provided a method of making a compostable package for containing a liquid or a liquid containing material comprising, providing a base of paperboard, coating said paperboard with a material capable of preventing leaks, wherein said base and said material are compostable to carbon dioxide, water and

biomass, forming said paperboard into a container and sealing the edges and bottom of said container.

In still another aspect of the invention there is provided a method of using a compostable package for containing a liquid or a liquid containing material comprising, providing a base of paperboard, coating said paperboard with a material capable of preventing leaks, wherein said base and said material are compostable to carbon dioxide, water and biomass, forming said paperboard into a container, sealing the edges and bottom of said container, and placing into said container a liquid or a material containing a liquid.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

Brief Description of the Drawings

Figure 1, illustrates the aerobic biodegradation of polycaprolactone using ASTM D5209.

Figure 2, illustrates the loss of mechanical properties observed for a film of polycaprolactone under outdoor composting conditions.

Figure 3, illustrates the loss of mechanical properties observed for a film of polycaprolactone under indoor composting conditions.

Figure 4, illustrates the biodegradability mechanism for polycaprolactone.

Figure 5, illustrates the biodegradations of polyesters of 3-hydroxybutyric acid and 3-hydroxyvaleric acid (PHBV).

Figure 6, illustrates the aerobic biodegradation of blends of polycaprolactone and polyethylene.

Figure 7, illustrates the loss of mechanical properties observed for a film of polycaprolactone - polyethylene blends under outdoor composting conditions.

Figure 8, illustrates the loss of mechanical properties observed for a film of polycaprolactone - polyethylene blends under indoor composting conditions.

Figures 9-12, illustrate cross-sectional views of the structure of the container materials according to the present invention.

Figure 13, illustrates the apparatus for use in the test methodology employed in the examples.

Best Mode for Carrying Out the Invention

According to the present invention, a paperboard container is produced for containing liquids or liquid containing materials. The container is formed from paperboard or related paper substrates. For the purposes of this invention, the term paperboard refers to those grades and types of paper made on either cylinder board machines or multiwire, fourdrinier type machines as well as multiformers. Fiber stock may be either recycled, or virgin or mixtures thereof, bleached or unbleached. Additional information on paper and paperboard used in packaging applications may be found in James E. Kline, Chapter 10, Paper and Paperboard, Miller Freeman Publications, San Francisco, CA, 1982.

The paperboard or paper substrate for use in the present invention has a basis weight of from about 35 lbs/ream to about 220 lbs/ream and preferably from about 175 lbs/ream to about 220 lbs/ream. According to one embodiment of the present invention, the paper substrate has a thickness from about 4 to 25 mils and more preferably about 10 to 20 mils. The coated paperboard should be selected to produce a container having a cross directional (CD) stiffness as determined by the Taber method of from 50 to 150 and more preferably of from 60 to 135. The Taber method is described in TAPPI Test Procedure T-489.

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The ratio of cross direction Taber stiffness of the coated paperboard to its basis weight (lb/ream) is at least 0.20 and more preferably at least 0.5.

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Paperboard is generally stronger and stiffer in the machine direction (MD) than in the cross direction. According to one embodiment of the present invention the machine direction preferably runs along the container from side to side, i.e. in a direction perpendicular with the top and bottom of the container. The machine direction runs from side to side of the container; the fiber direction of the paperboard from top to bottom of the container is said to be the cross direction (CD). The coated paperboard used in the container according to the present invention preferably has a ratio of Taber stiffness of MD/CD of less than or equal to about 2.65 and more preferably less than or equal to about 1.92.

The paperboard or paper substrate material is coated on at least one side thereof with a degradable resin in a thickness of from about 0.5 to 2.0 mils. In one preferred embodiment, both sides of the paperboard substrate are coated with the degradable resin to a thickness of from about 0.5 to about 2.0 mils. In the present invention degradation includes biodegradation as well as degradation by moisture, light, oxygen and other well known means of breaking down waste materials.

Coating techniques, for example, extrusion coating, impregnation and the like, are well known in the art, and in accordance with the present invention, inner coatings and outer coatings may be applied by processes well known in the art. Furthermore, the design, quality control and fabrication of folded cartons for the containment of liquids are well known in the art, and these processes and techniques may be used in making the containers of the present invention.

Characteristics of the biodegradable coating materials for use in the present invention include good moisture barrier properties, good thermal sealing properties, sufficient stiffness to give the container good crush resistance and biodegradability under composting conditions.

Examples of biodegradable resins include thermoplastic oxyalkanoyl polymers, e.g., ϵ - caprolactone polymers and those that contain the recurring unit:

$$-O(CH_2)_x-C=O$$

Wherein x is an integer having a value of 2,3 and 5-7, including polymers of beta propriolactone and Δ - valerolactone; polyesters of 3-hydroxybutyric acid, 3-hydroxyvaleric acid and mixtures thereof as well as copolymers of any of the above.

Suitable also are graft polymers prepared by reacting a lactone such as ϵ - caprolactone with hydroxyl or amino functional resins such as hydrolyzed ethylene - vinyl acetate copolymers; segmented polyurethane prepared by reacting polycaprolactone bearing terminal hydroxyl groups with diisocyanates and, optionally, chain-extending glycols such as 1,4 butanediol.

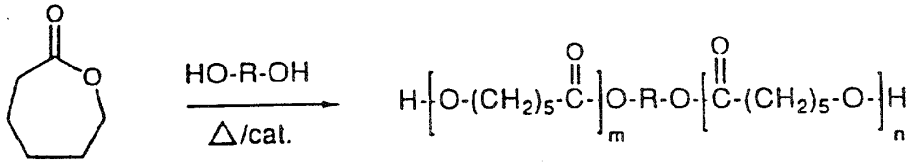
Included also are aliphatic polyesters such as polyglycolic acid, polylactic acid, polydioxanone, poly(trimethylene carbonate) and their co- and terpolymers as well as blends of any of the above with polyesters prepared from alkanediols and alkanedicarboxylic acids including oxalates.

Preferred biodegradable resins for use in the present inven
tion are polyhydroxyaliphatic acids (PHAA).

Naturally occurring biodegradable substances are useful as fillers offering the advantage of reduced cost. Such fillers include starch, tree bark, ground paper, peat moss and soy bean powder.

Polyhydroxyaliphatic acids in film form are biodegradable under composting conditions. One preferred polyhydroxyaliphatic acid, polycaprolactone (PCL) is

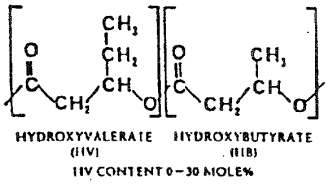
available as a biodegradable thermoplastic resin from Union Carbide. It is synthesized from ϵ-caprolactone:




Polycaprolactone in film form, has been demonstrated to be biodegradable under soil burial and composting conditions, as shown in Figures 1-3. Composting of PCL is thought to occur by the mechanism proposed in Figure 4.

Other preferred polymers for use in the present invention are the commercially available PHBV polymers of ICI which are polyesters of 3-hydroxybutyric (HB) and 3 hydroxyvaleric (HV) acids. Their general structure is:

PHBV COPOLYMERS




These polymers are produced by the fermentation of sugar by the bacterium ALCALIGENES EUTROPHUS and will degrade to carbon dioxide and water when placed in the presence of microorganisms found in soil, sewage, and river bottoms as shown in Figure 5.

While PCL is claimed to undergo aerobic degradation, PHBV will degrade under either aerobic or anaerobic conditions.

To enhance or optimize functional properties and cost it may be desirable to blend these resins with other material. The successful blending of the aliphatic polyester with additives to provide improved properties and reduced cost without impairing degradability was a most useful and surprising aspect of this invention.

Additives and blending resins include those which are either miscible or mechanically compatible with aliphatic polyester. Examples listed below are suitable for use with polycaprolactone:

| Miscible | Mechanically Compatible |
|---|---|
| PVC | Polyethylene |
| SAN | Polypropylene |
| ABS | Natural Rubber |
| Phenoxy | Styrene/Butadiene |
| Polycarbonate | Elastomer & Block Copolymers |
| Nitrocellulose | Polyvinylacetate |
| Poly (Vinylidene Chloride) | Polybutadiene |
| Styrene/Allyl Alcohol Copolymers | Ethylene/Propylene Rubber |

In addition, PCL may be blended with thermoplastic elastomers for improved toughness, adhesive, and flexibility. Especially suitable are the elastomeric segmented polyurethanes prepared from aliphatic polyester diols, aromatic or alicyclic diisocyanates; and, optionally, short chain diol or diamine chain - extender.

Accordingly, the skilled artisan can incorporate the many useful and unique properties of these additives into the coating composites to meet specific requirements of the various end uses contemplated. These materials may be added in from about 0% to about 30%, preferably from about 10 to about 20%. Although these materials alone are either slowly compostable or noncompostable, their use in limited amounts as described above does not impair the ultimate biodegradation of the coating materials.

In addition to blended compositions, these compositions may be coated onto the paperboard substrate in successive layers. Noncompostable or slowly compostable layers are so positioned so as not to interfere with composting of the remainder of the container. As an alternative, individual layers of the same or different blended materials may be used to form the substrate coatings. Noncompostable and slowly compostable materials may be used in blends or as intermediate layers in limited amounts. When used in blends,

these materials are preferably contained in less than 30% and when found in film form are preferably less than o.6 mils in thickness. These materials do not interfere with the compostability and degradation of the container and are found in the humus. After composting, these materials are from a practical standpoint indistinguishable from the rest of the humus.

In one preferred embodiment, the coating is comprised of either 100% aliphatic polyester or mixtures thereof with polyethylene in which the polyethylene is present at levels up to about 30%. The addition of polyethylene reduces the rate of water vapor transmission which is advantageous for certain long shelf-life products. With the addition of as much as 30% polyethylene to aliphatic polyester, composting is slower, but nevertheless effective under typical composting conditions, as shown in Figures 6-8.

As an alternative or in addition to the materials described above, starch may be added to the coating materials according to the present invention. Starch may be added in from about 0% to about 70% and more preferably from about 40 to about 60%. One commercially available starch based biodegradable material for use in the present invention is Mater-Bi® produced by Novamont. This product contains up to 60% starch and 40% of a biodegradable resin material.

Since both coatings and pulp-based substrate are degradable, disposable packages from these composites will decompose completely thus contributing to alternate waste treatment of paper based products. In addition to being completely degradable, the containers according to the present invention may be incinerated.

Figures 9, 10, 11, and 12 show several embodiments of the coated paperboard used in the production of the container according to the present invention.

In Figure 9, layer 1 is a flexible, strong paper substrate. Layer 2 is an interior or exterior coating of 80-100% of a biodegradable resin having a thickness of from about 0.5 to about 2.0 mil.

In Figure 10, layer 1 is a paperboard substrate. An interior coating 2 and an exterior coating 3 are each present at a thickness of from about 0.5 to about 2.0 mil.

When it is desirable to minimize the rate of water vapor transmission, the coated paperboard illustrated in Figure 11 or 12 can be employed. In Figure 11, a layer 4 comprising a barrier layer, for example a high polyethylene content (30-100%) layer is coated directly onto one side of the paperboard. This coating is less than 0.5 mil. in thickness and preferably about 0.2-0.3 mil.

In one preferred embodiment, coatings 2 and 3 are comprised of at least 70% and preferably 90-100% of aliphatic polyester at a thickness of from about 0.5 to about 2 mils each. In addition to meeting all of the requirements described in (a)-(f) above, this embodiment provides an excellent barrier to moisture vapor. The polyethylene component which represents only about 1-3% by weight of the total composition does not interfere with the rate of composting as it is confined to the innermost layer and therefore does not hinder the degradation of the outermost layers, i.e.: the aliphatic polyester or the cellulose pulp fibers. Thus, in this embodiment of the invention, the outer surfaces 2 and 3, which provide the initial sites for microbial attack, are composed of the biodegradable aliphatic polyester coatings. The pulp substrate 1 is accessible to microbial attack either through the degraded layer 3 or through the edges.

In another alternative, the exterior coating layer 3 may be eliminated in which case exposure of the pulp layer is immediate and direct.

Figure 12 represents an alternate configuration to the performance properties and compostability of Figure 10. In this particular case, the high barrier layer 4 is positioned between two layers of pulp substrate 1 and 1'.

The container according to the present invention can be used to contain a variety of liquids and liquid containing materials. For Example, the container may be used for

beverages such as milk, juice, fruit punch, soda, frozen juice, and iced tea; fabric softener; butter; margarine; cosmetics such as shampoo, conditioner, suntan lotion and body lotion; pancake syrup; cooking oil; processed grains, fruits and vegetables such as applesauce and pasta sauces; frozen vegetables; fruits; breads and bread products and single-use wet wipes.

In one embodiment, the container which is preferable for use with the present invention has cut ends which are sealed to avoid seepage of the liquid into or out of the body of the paperboard. The sealing of the edges may be done in a variety of manners. It may be accomplished by coating the edges, or by thinning the material down near the cut edges, i.e., skivving. Skivving of the edges is followed by folding the skivved areas over the cut edges.

In another preferred embodiment, there is a moisture-impervious membrane provided over the contents. Such membranes are sometimes referred to as lidding stock or material. Membranes for this application are typically comprised of a strong barrier top layer with a heat sealable lower layer. Non-limiting examples of top layers which may be used in the present invention, include paper, polyester, polyethylene, metallized polyester and polypropylene. Non-limiting examples of heat seal layers include polyethylene, ethylene-vinylacetate copolymers, and aliphatic polyester. The edges of the membrane are adhered to the upper edges of the container and provide an effective storage and shipping seal. The membrane should peel away from the edges of the container at the seal without exposure of pulp fibers. Additionally a moisture-impervious membrane can be heat sealed at the bottom of the container as well. The bottom of the container is preferably heat sealed by applying heat and pressure, as well known in the art.

In one embodiment when the material to be contained is wet towellettes, the consumer obtains the product, rips open a perforation providing a slot or opening in the paperboard, permitting the hinged cap-like lid to be raised. This

exposes the membrane, which is easily peeled off with the fingers and either stored in the box or thrown away. Thereafter, sealing is done entirely by the raising and lowering of the hinged lid. The moist towels or napkins are preferably stacked and lie horizontally in the container and may be individually removed as needed.

It is also possible to provide a separate or separable pouch, bag or liner within the container to provide further waterproofing protection. Alternatively, this separable liner may be supplied during refilling of the container using a prepackaged bag of replacement wipes.

The container according to the present invention provides sufficient stiffness to provide the consumer with a container having handleability and to provide crush resistance of the box during storage, shipment and under conditions of household use.

Containers according to the present invention preferably have a compression strength of at least 60 lbs. and more preferably at least 70 lbs. as tested in accordance with TAPPI test procedure T-804. The container should also preferably have a cross directional Ring Crush of at least 115 lbs. and more preferably at least 140 lbs. Ring crush can be defined according to TAPPI Test Procedure T818 om-87. The compression strength of the containers is indicative of stacking and handling ability of the containers. Higher stiffness and crush resistance in the cross direction of the paperboard provides improved stacking and handling of the containers.

The following examples are illustrative of the invention embodied herein.

EXAMPLES

I. Paper used as base:

a. Bleached paperboard grade DLC (Schoeller Technical Papers, Pulaski, N.Y.); basis weight 175 lb/ream, 11.5 mils in thickness. Taber Stiffness MD (machine direction) x CD (cross direction) = 65 x 35.

b. Bleached paperboard grade 4554 (Westvaco); basis weight 205 lb/ream; 20 mil in thickness.

c. Bleached paperboard grade GAA-11 (Schoeller) 3.5 mil., 38 lb/ream.

d. Bleached paperboard 215 lb/ream, International Paper.

II. The coatings were extruded from the following polymers:

a. polycaprolactone (PCL) Tone Polymers P-767E and P-787 (representing different molecular weights with 767E being the lowest), Union Carbide Chemicals and Plastics Company, Inc., Solvents and Coatings Materials Division, Bound Book, N.J.

b. PHBV tm (ICI Americas, Wilmington, DE) - 8% and 12% polyhydroxyvalerate;

c. Linear low density polyethylene (LLDPE); hexene based grade DFDA-7047 (Union Carbide)

d. Low density polyethylene (LDPE) (Quantum)

III. Testing and Evaluations

a. Liquid containment was evaluated by the Mason Jar Test as follows:

**The Mason Jar Test to Determine Liquid Containment of Packaging Materials**

This test procedure provides a convenient way to observe the liquid barrier properties of film, paper, coated paper and related packaging materials. Failure in the test materials such as attack or penetration by the contained liquid or leaks through pin-holes and other coating imperfections are usually observed within the first 24 hours of the test.

As can be seen from Figure 13, a standard wide mouth Ball type Mason Jar, 7 inch high and 3½ inch wide is drilled with a 1/8" hole for pressure equalization.

The hole is plugged and the jar is filled with 600 ml of liquid. Optionally, dye may be added to aid in observing the nature and location of failures.

Test specimen circles 3 and 5/16" in diameter are placed between two rubber gaskets and then tightened on the jar with the outer screw type lid supplied with the jar.

The jar is inverted and the plug removed.

The assembly is examined daily for signs of leakage and penetration.

In those cases where fluid consistently leaked around specimen edges, it was useful to heat seal the material to the rubber gaskets.

Test results are reported based upon sample composition, thickness, liquid, elapsed time and nature of failure.

b. Water vapor transmission (WVT) was measured according to TAPPI T523 on -87 and ASTM F 1249-90

c. Oxygen transmission was measured according to ASTM D-3985

Extrusion coatings were conducted using an Egan single flight screw through a 15 inch T-type die with a 30 mil gap setting.

Polycaprolactone P-767E was extruded with a temperature profile of 200°F in the feed zone; 225-250°F in the barrel and 245°F in the die.

Films were collected on a matte finished steel chill roll at 55-60°F and combined through a nip roll with the substrate after surface treatment of the latter with corona discharge or flame to enhance adhesion.

EXAMPLE 1

PCL-767E was coated on one side of the Westvaco paperboard at a thickness of 1.25 mils. The coated material was challenged with baby wet wipe lotion in the Mason Jar Test with no signs of penetration or leakage after one month. Its water vapor transmission rate was 15.65 gm/100 sq.in./24 hr.

EXAMPLE 2

The coated paperboard from Example 1 was coated on the other side with a second layer of PCL-767E at 1.25 mil.

The coated board basis weight was 311.5 g/sq.m. with a thickness of 23 mils.

In the Mason Jar Test, using Downy® Fabric Softener, manufactured by Proctor & Gamble, as the fluid, no leaks, swelling or penetration was observed after 1.3 months. Similar results were observed with iced tea over a period of 26 days. Water vapor transmission was 8.55 gm/100 sq.in./24 hr.

EXAMPLE 3

PHBV 8% and 12% were mixed in a 1:1 ratio and extruded on the DLC substrate at a thickness of 1.5 mil. The basis weight of the coated paper was 215.8 g/sq.m.

In the Mason Jar Test, this material resisted leakage penetration by baby wet wipe lotion for two months.

EXAMPLE 4

The coating mix of Example 3 was applied to one side of the DLC substrate at a thickness of 2.0 mil. Total basis weight was 241.8 g/sq.m. The water vapor transmission value was 4.5 gm/100 sq.in./24 hr.

EXAMPLE 5

Polycaprolactone P-767E and LLDPE resin were mixed in a ratio of 90% PCL and 10% LLDPE and extruded onto the Westvaco paperboard at a coating thickness of from about 1.0 to about 1.3 mil.

Extrusion temperatures were 275°F at the feed zone 325-345°F in the barrel; and 345°F in the die.

Basis weight was 291.5 g/sq.m. Water vapor transmission was 11.0 gm/sq.in./24 hr. In comparison to Experiment 1, water vapor transmission was reduced by 30% due to the presence of the polyethylene.

EXAMPLE 6

In this experiment a second coating layer was applied to the product of Example 5. Coating thickness was 1.25 mil. and the basis weight measured at 303.9 g/sq.m. Water vapor transmission was 5.33 gm/100 sq.in./24 hrs. In comparison to Experiment 2, water vapor transmission was reduced by 38% due to the presence of polyethylene.

In the Mason Jar Test with baby wet wipe lotion, no leaks or penetration was observed for five weeks.

EXAMPLE 7

PCL-767E and LLDPE were mixed in a ratio of 85/15 and extruded onto the Westvaco* paper at a thickness of 1.25 mil. Water vapor transmission was 8.45 gm/100 sq.in./24 hr. In comparison to Experiment 1, water vapor transmission was reduced by 46% due to the polyethylene.

Downey fabric softener was used in the Mason Jar Test with no leaks or penetration after one month.

EXAMPLE 8

A second layer of 85/15 PCL-767E and LLDPE at 1.25 mil. was applied to the other side of the substrate used in Experiment 7 giving a total basis weight of 300.7 g/sq.m.

Water vapor transmission was 4.81 gm/100 sq.m./24 hr. In the Mason Jar Test with baby wet wipe lotion, no leaks or penetration was observed for three weeks. In comparison with Experiment 2, water vapor transmission was reduced by 44% due to the presence of polyethylene.

Examples 1-8 above illustrate the configurations as set forth in Figures 9 and 10.

EXAMPLE 9

With DLC as the substrate an 0.5 mil. coating of low density polyethylene (Quantum NA-206) was extruded on one side only.

Two layers of PCL-767E at 1.2 mil. each were then

*Trade-mark

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extruded onto first, the polyethylene side and second, the uncoated side. This composite is representative of the embodiment described in Figure 10. The water vapor transmission rate was 1.22 gm/100 $in^2$/24 hr.

EXAMPLE 10

Example 9 was repeated with a polyethylene coating of 0.3 mil. The water vapor transmission rate was 1.79 gm/100 $in^2$/24 hr. Taber Stiffness according to TAPPI-489 was 98.5 in the machine-direction and 60.0 in the cross direction.

EXAMPLE 11

This is an example of the configuration shown in Figure 8. The substrate, GAA-11, was a high tear strength, starch sized paper at 3.5 mil. thickness. It was extrusion coated with 2.0 mil. of PCL-767E giving a material useful as a heat sealable lidding stock.

The following examples illustrate test samples which were deemed to provide acceptable barrier properties and degradation properties for use in the present invention.

Example 12

2.0 mils of 85% PCL and 15% LLDPE was coated on both sides of a base of 215 lb/ream paperboard obtained from International Paper.

Example 13

1.25 mils of 85% PCL and 15% LLDPE was coated on both sides of a base of 215 lb/ream paperboard obtained from International Paper.

Example 14

2.0 mils of 90% PCL and 10% LLDPE was coated on both sides of a base of 215 lb/ream paperboard obtained from International Paper.

Example 15

1.25 mils of 90% PCL and 10% LLDPE was coated on both sides of a base of 215 lb/ream paperboard obtained from International Paper.

Example 16

First 0.5 mils of LDPE and then 1.25 mils of PCL were coated on one side of a base of 215 lb/ream paperboard obtained from International Paper. The other side of the based was coated with 2.0 mils of PCL.

Example 17

0.5 mils of LDPE, 85% PCL and 15% Texin 480A polyurethane was coated on both sides of a base of 215 lb/ream paperboard obtained from International Paper.

The oxygen permeability of these and other coatings on paperboard are compared in the chart below (23°C):

| COATING SAMPLE | CC $O_2$/100 $IN_2$/24 HOUR | |
|---|---|---|
| | 760 mm $O_2$ | Omm $O_2$ |
| Low density polyethylene; reference Example 3 Serial No. 07/923,556 | 21.8 (80% RH) | 17.2 (80% RH) |
| | 22.2 (30% RH) | 17.3 (30% RH) |
| Example 2 Present Invention | 13.8 (80% RH) | 12.6 (80% RH) |
| | 13.8 (30% RH) | 12.4 (30% RH) |
| Example 6 | 29.0 (80% RH) | 16.5 (80% RH) |
| | 33.0 (30% RH) | 43.0 (30% RH) |
| Example 8 | 26.0 (80% RH) | 15.4 (80%) |
| | 30.4 (30% RH) | 28.5 (30% RH) |

The coated paper board materials described in the examples above are excellent candidates in the construction of containers for the packaging of liquids and wet products.

Ease of sealing and seal integrity were excellent, and surprisingly better than polyethylene which is the current industry standard. When exposed to hot air for 5-10 seconds, these coatings became tacky and readily formed strong coating to coating or coating to paper bonds. The present invention also provides for means by which the adhesive properties of the coated surface may be modified. For examples, in the opening and dispensing of a heat sealed container, the adhesion may be desirably reduced to allow a clean, fiber-free peel and separation of layers.

These and related modifications may be achieved by blending or by topical treatment of the coatings described herein with low molecular weight, (i.e., 500-3000) aliphatic polyesters. The later have a tendency to be waxy and low in strength; and, as such, weaken the adhesive interface and lower the cohesive strength of the coating.

Materials of this invention are well suited to the steps involved in converting coated paperboard into a folded carton including sheeting, printing, scoring, perforating, skivving, folding, and sealing.

The result of the Mason Jar Tests with typical fluids indicate that aliphatic polyesters in film form when coated on paper substrates are entirely satisfactory in containing a wide range of liquids.

Other embodiments of the invention will be invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

CLAIMS:

1. A compostable container for packaging a liquid or liquid containing material comprising:

a base of paper board having an internal surface and an external surface;

at least the internal surface treated with a corona discharge or a flame; and

a coating material selected from aliphatic polyesters to a thickness of from 0.5 mil to 2.0 mil applied to at least the internal surface;

wherein the base and the coating material are capable of degrading at substantially the same rate to form carbon dioxide, water and biomass; and

wherein the base has a cross-directional Taber stiffness of 50 to 150, a thickness of from 4 to 25 mils, and a basis weight of from 25 to 220 lbs./ream.

2. The container according to claim 1, wherein the coating material is heat sealable, flexible, adhesive, resistant to stress cracks and abrasion resistant.

3. The container according to claim 1 or 2, wherein the coating material is selected from polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid and copolymers of glycolic acid, lactic acid and polyactide.

4. The container according to claim 3, wherein the coating material is polycaprolactone.

5. The container according to any one of claims 1 to 4, wherein said coating material further contains an additive

selected from the group consisting of PVC, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, poly vinylidene chloride, styrene/allyl alcohol copolymers, polyethylene, polypropylene, natural rubber, styrene/butadiene elastomer and block copolymers, polyvinylacetate, polybutadiene, ethylene/propylene rubber, starch and thermoplastic segmented polyurethane.

6. The container according to claim 5, wherein the additive is polyethylene.

7. The container according to any one of claims 1 to 6, wherein said base further comprises, two layers of paperboard having a barrier layer placed therebetween.

8. The container according to claim 7, wherein the barrier layer is polyethylene.

9. The container according to any one of claims 1 to 6, wherein said base of paperboard has a barrier layer applied prior to application of said coating material.

10. The container according to claim 9, wherein the barrier layer is polyethylene.

11. A method of making a compostable package for containing a liquid or liquid containing material comprising the steps of:

providing a base of paper board having an internal and an external surface;

treating at least the internal surface with a corona discharge or a flame; and

coating at least the internal surface with a coating material selected from aliphatic polyesters capable of preventing leaks to a thickness of from 0.5 mil to 2.0 mil;

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wherein the base and the polyester coating material are capable of degrading at substantially the same rate to form carbon dioxide, water and biomass; and

wherein the base has a cross directional Taber stiffness of 50 to 150, a thickness of from 4 to 25 mil, and a basic weight of from 25 to 220 lbs./ream; and

forming the coated paper board into a container;

filling the container with a liquid or liquid containing material therein; and sealing said container.

12. The method according to claim 11, wherein the coating material is heat sealable, flexible, adhesive, resistant to stress cracks and abrasion resistant.

13. The method according to claim 11 or 12, wherein the coating material is selected from polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid and copolymers of glycolic acid and lactic acid.

14. The method according to claim 13, wherein the coating material is polycaprolactone.

15. The method according to any one of claims 11 to 14, wherein said coating material further contains an additive selected from the group consisting of PVC, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, poly vinylidene chloride, styrene/allyl alcohol copolymers, polyethylene, polypropylene, natural rubber, styrene/butadiene, elastomer and block copolymers, polyvinylacetate, polybutadiene, ethylene/propylene rubber and starch.

16. The method according to claim 15, wherein the additive is polyethylene.

17. The method according to any one of claims 11 to 16, wherein the liquid or liquid containing material is selected from the group consisting of milk, juice, fruit punch, soda, frozen juice, iced tea, fabric softener, butter, margarine, cosmetics, shampoo, conditioner, suntan lotion, body lotion, pancake syrup, cooking oil, processed grains, fruits, vegetables, applesauce, pasta sauces, frozen vegetables, frozen fruits, breads, bread products and single-use wet wipes.

18. The method according to claim 17, wherein the liquid or liquid containing material is single-use wet wipes.

19. A method of using a compostable container for packaging a liquid or liquid containing material comprising the steps of:

providing a base of paper board having an internal and an external surface;

treating at least the internal surface with a corona discharge or a flame; and

coating at least the internal surface with a coating material selected from a polyhydroxyaliphatic acids capable of preventing leaks to a thickness of from 0.5 mil to 2.0 mil;

wherein the base and the coating material are capable of degrading at substantially the same rate to form carbon dioxide, water and biomass; and

wherein the base has a cross directional Taber stiffness of 50 to 150, a thickness of from 4 to 25 mil, and a basis weight of from 25 to 220 lbs./ream; and

forming the coated paper board into a container;

sealing the edges and bottom of the container;

and placing into the container a liquid or a material containing a liquid.

20. The method according to claim 19, wherein the coating material is sealable, flexible, adhesive, resistant to stress cracks and abrasion resistant.

21. The method according to claim 19 or 20, wherein the coating material is selected from polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid and copolymers of glycolic acid, lactic acid and polyactide.

22. The method according to claim 21, wherein the coating material is polycaprolactone.

23. The method according to any one of claims 19 to 22, wherein said coating material further contains an additive selected from the group consisting of PVC, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, poly vinylidene chloride, styrene/allyl alcohol copolymers, polyethylene, polypropylene, natural rubber, styrene/butadiene, elastomer and block copolymers, polyvinylacetate, polybutadiene, ethylene/propylene rubber and starch.

24. The method according to claim 23, wherein the additive is polyethylene.

25. The method according to any one of claims 19 to 24, wherein the liquid or liquid containing material is selected from the group consisting of milk, juice, fruit punch, soda, frozen juice, iced tea, fabric softener, butter, margarine, cosmetics, shampoo, conditioner, suntan lotion, body lotion, pancake syrup, cooking oil, processed grains, fruits, vegetables, applesauce, pasta sauces, frozen vegetables, frozen fruits, breads, bread products and single-use wet wipes.

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26. The method according to claim 25, wherein the liquid or liquid containing material is single-use wet wipes.

27. A compostable package for liquid or liquid containing material comprising:

a base of paper board having an internal surface and an external surface;

at least the internal surface treated with a corona discharge or a flame; and

a coating material selected from polyhydroxyaliphatic acids capable of preventing leaks to a thickness of from 0.5 mil to 2.0 mil applied to at least the internal surface;

wherein the base and the coating material are capable of degrading at substantially the same rate to form carbon dioxide, water and bio mass;

wherein the base has a cross-directional Taber stiffness of 50 to 150, a thickness of from 4 to 25 mils,

and a basis weight of from 25 to 220 lbs./ream.

28. The container according to claim 27, wherein the coating material is sealable, flexible, adhesive, resistant to stress cracks and abrasion resistant.

29. The container according to claim 27 or 28, wherein the coating material is selected from polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid and copolymers of glycolic acid and lactic acid.

30. The container according to claim 29, wherein the coating material is polycaprolactone.

31. The container according to any one of claims 27 to 30, wherein said material further contains an additive selected from the group consisting of PVC, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, poly vinylidene chloride, styrene/allyl alcohol copolymers, polyethylene, polypropylene, natural rubber, styrene/butadiene, elastomer and block copolymers polyvinylacetate, polybutadiene, ethylene/propylene rubber and starch.

32. The container according to claim 31, wherein the additive is polyethylene.

33. The container according to any one of claims 27 to 32, wherein the liquid or liquid containing material is selected from the group consisting of milk, juice, fruit punch, soda, frozen juice, iced tea, fabric softener, butter, margarine, cosmetics, shampoo, conditioner, suntan lotion, body lotion, pancake syrup, cooking oil, processed grains, fruits, vegetables, applesauce, pasta sauces, frozen vegetables, frozen fruits, breads, bread products and single-use wet wipes.

34. The container according to claim 33, wherein the liquid or liquid containing material is single-use wet wipes.

35. The container according to any one of claims 27 to 34, wherein said base further comprises, two layers of paperboard having a barrier layer placed therebetween.

36. The container according to claim 35, wherein the barrier layer is polyethylene.

37. The container according to any one of claims 27 to 34, wherein said base of paperboard has a barrier layer applied prior to application of said coating material.

38. The container according to claim 37, wherein the barrier layer is polyethylene.

# FIG. 1

AEROBIC BIODEGRADATION OF POLYCAPROLACTONE (ASTM D5209)

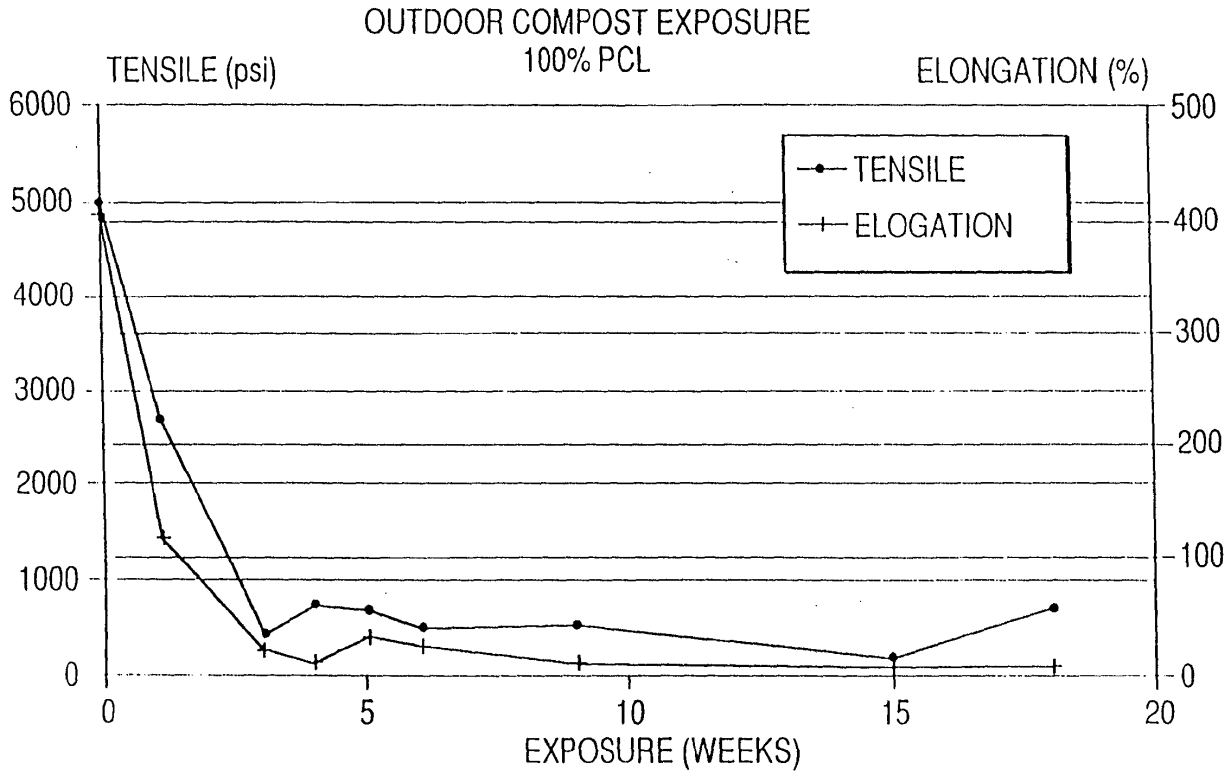
| INOCULUM EXPOSURE (DAYS) | CUMULATIVE CARBON DIOXIDE (mg) |
|---|---|
| 0 | 0 |
| 5 | 22.2 |
| 19 | 145.1 |
| 32 | 299.8 |
| 42 | 406.8 |
| 50 | 484.2 |
| 60 | 532.1 |



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FIG. 2




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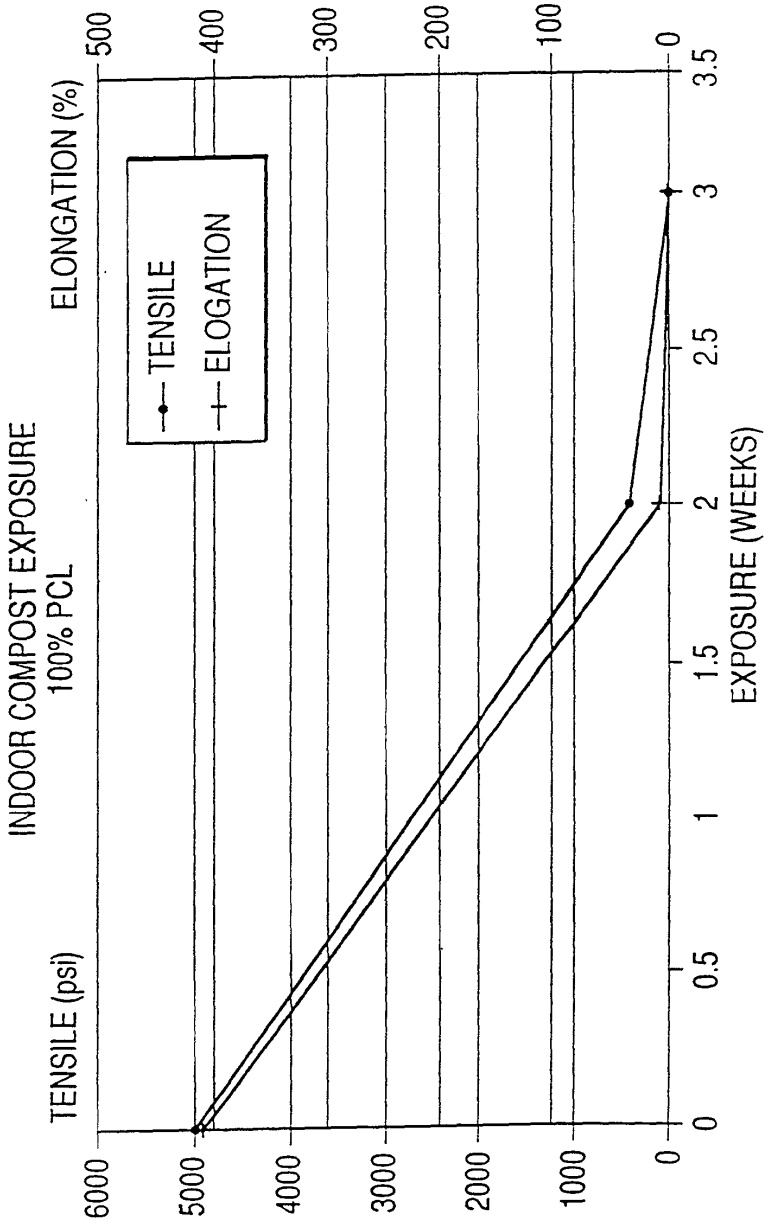
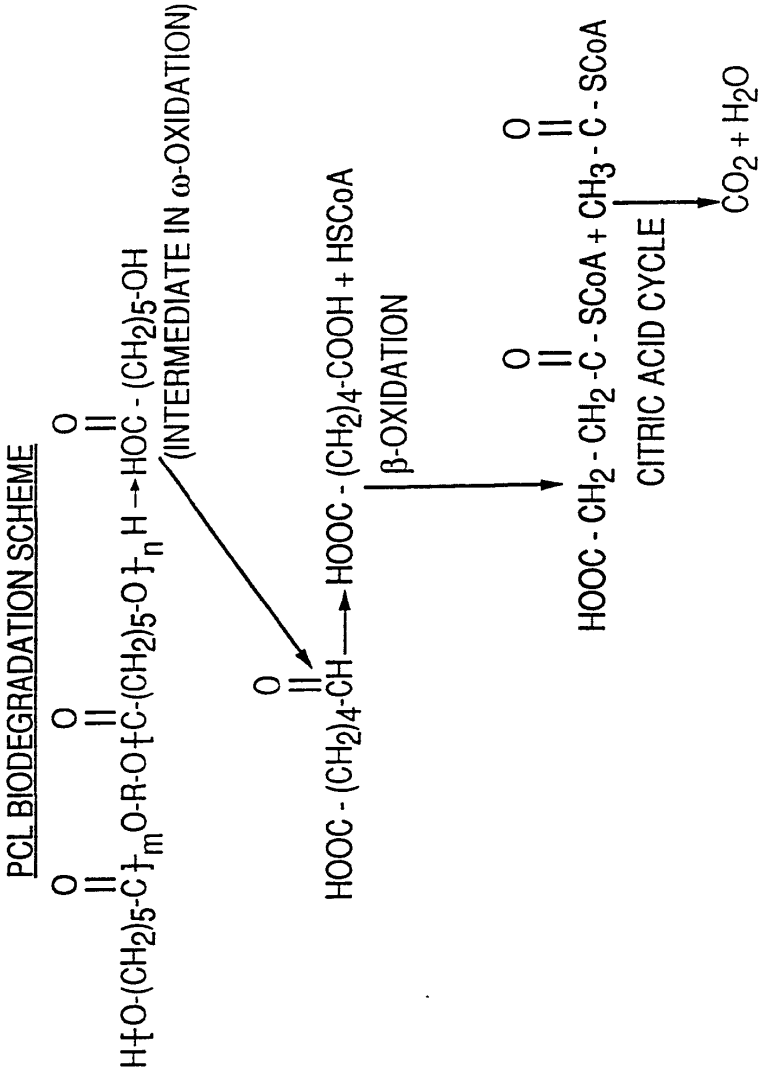



FIG. 3



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FIG. 4



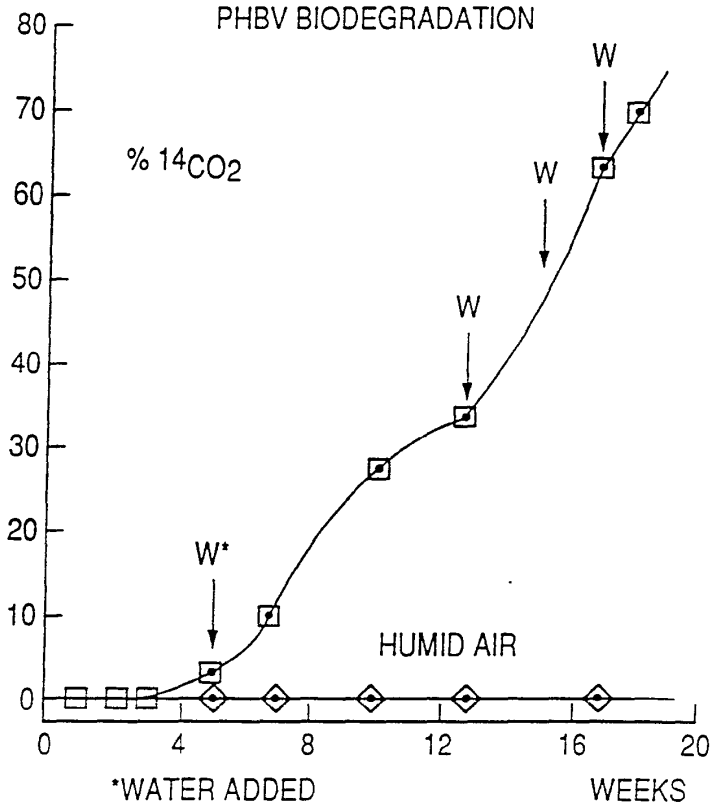



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## FIG. 5

PHBV IS INDEFINITELY STABLE WHEN STORED IN AIR; DEGRADATION TO $CO_2$ AND WATER WILL OCCUR ONLY WHEN THE POLYMERS ARE EXPOSED TO MICROORGANISMS FOUND NATURALLY IN SOIL, SEWAGE, RIVER BOTTOMS, ETC.

IN A CONTROLLED EXPERIMENT USING C14 TAGGED, PHBV FILM LOST APPROXIMATELY 50% OF ITS CARBON CONTENT IN 16 WEEKS AS $CO_2$ WHEN BURIED IN MOIST SOIL.






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*FIG. 6*

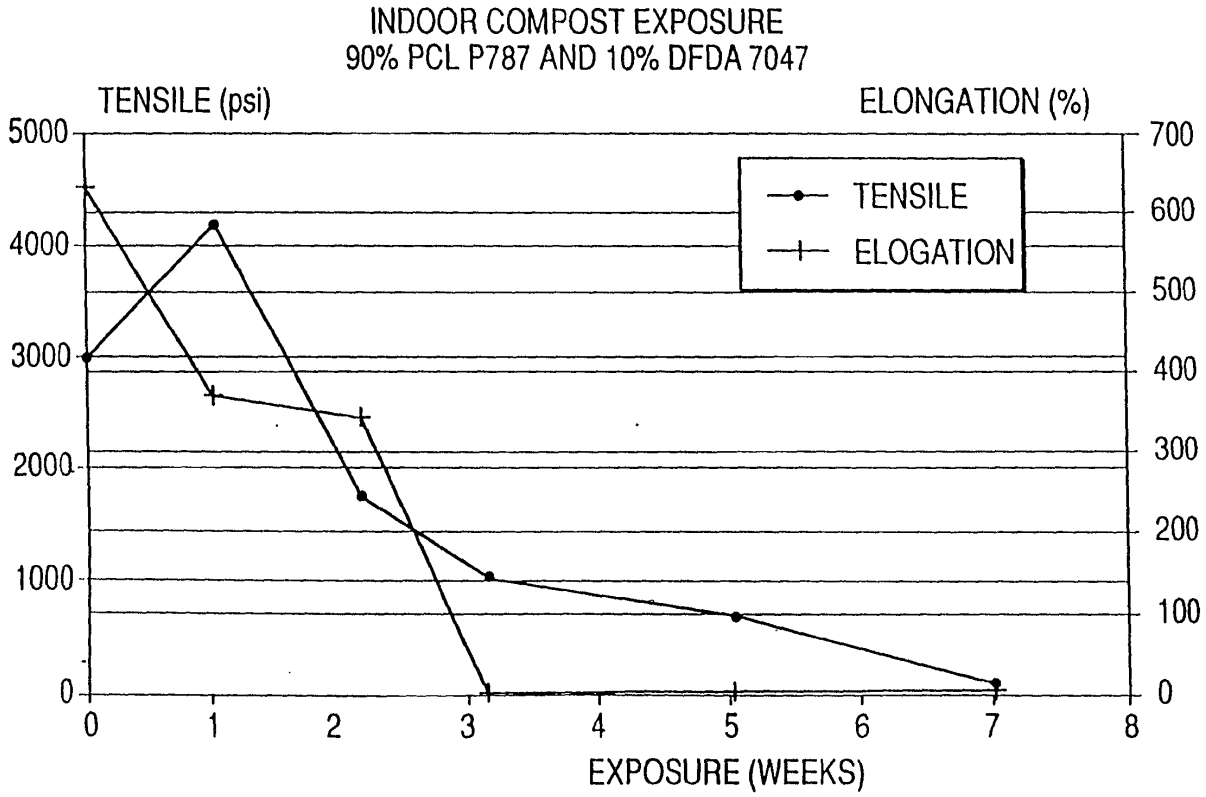
AEROBIC BIODEGRADATION OF
POLYCAPROLACTONE POLYETHYLENE BLENDS

| | CUMULATIVE CARBON DIOXIDE (mg) | |
|---|---|---|
| INOCULUM EXPOSURE (DAYS) | 90% PCL 10% LLDPE | 80% PCL 20% LLDPE |
| 0 | 0 | 0 |
| 5 | 24.6 | 19.8 |
| 19 | 228.9 | 125.8 |
| 32 | 361.0 | 198.4 |
| 42 | 391.8 | 220.4 |
| 50 | 406.3 | 256.3 |
| 60 | 440.5 | 287.8 |



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FIG. 7




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FIG. 8

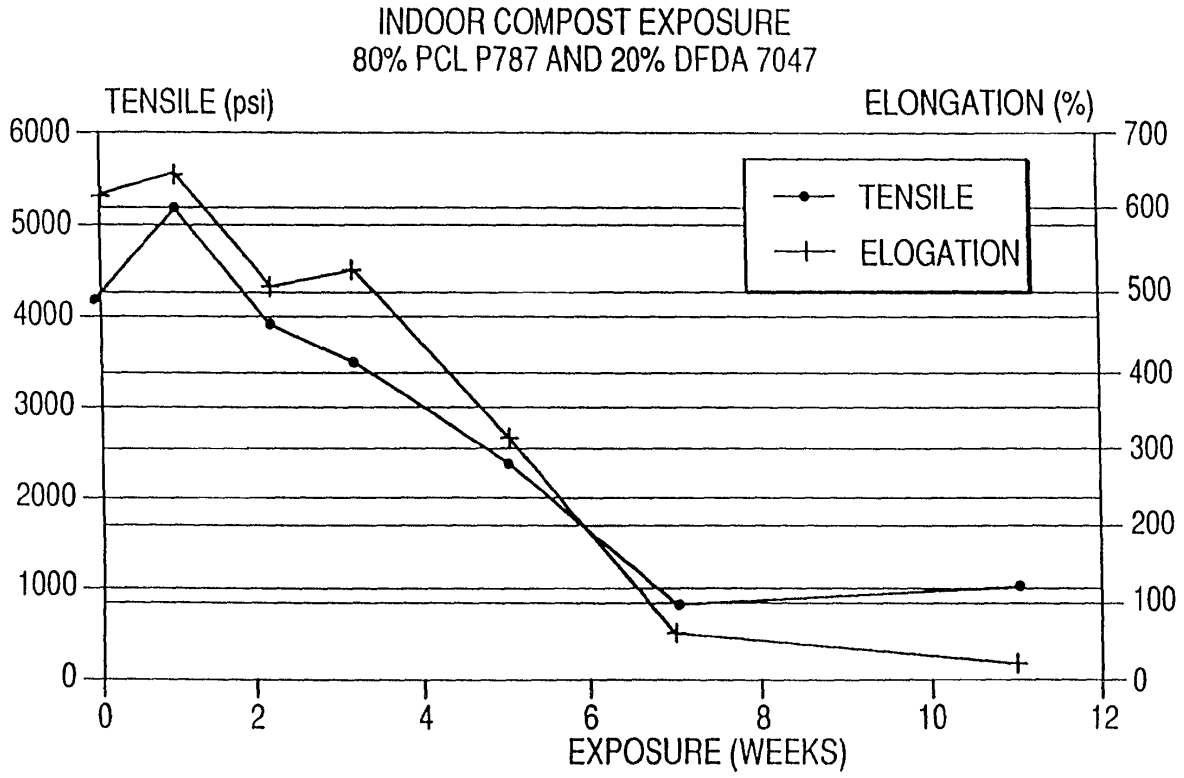


FIG. 9

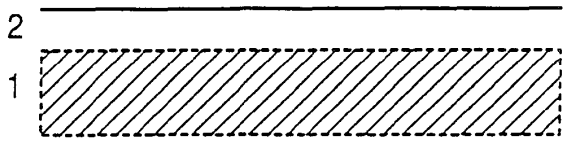



FIG. 10

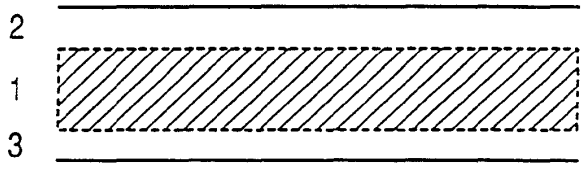



FIG. 11

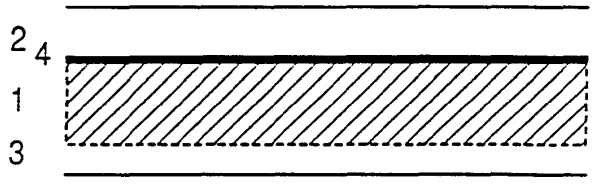
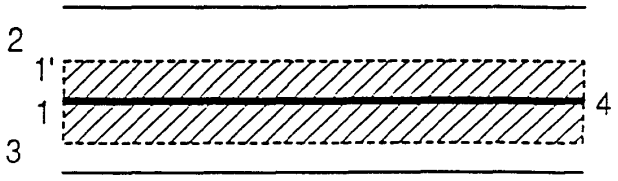


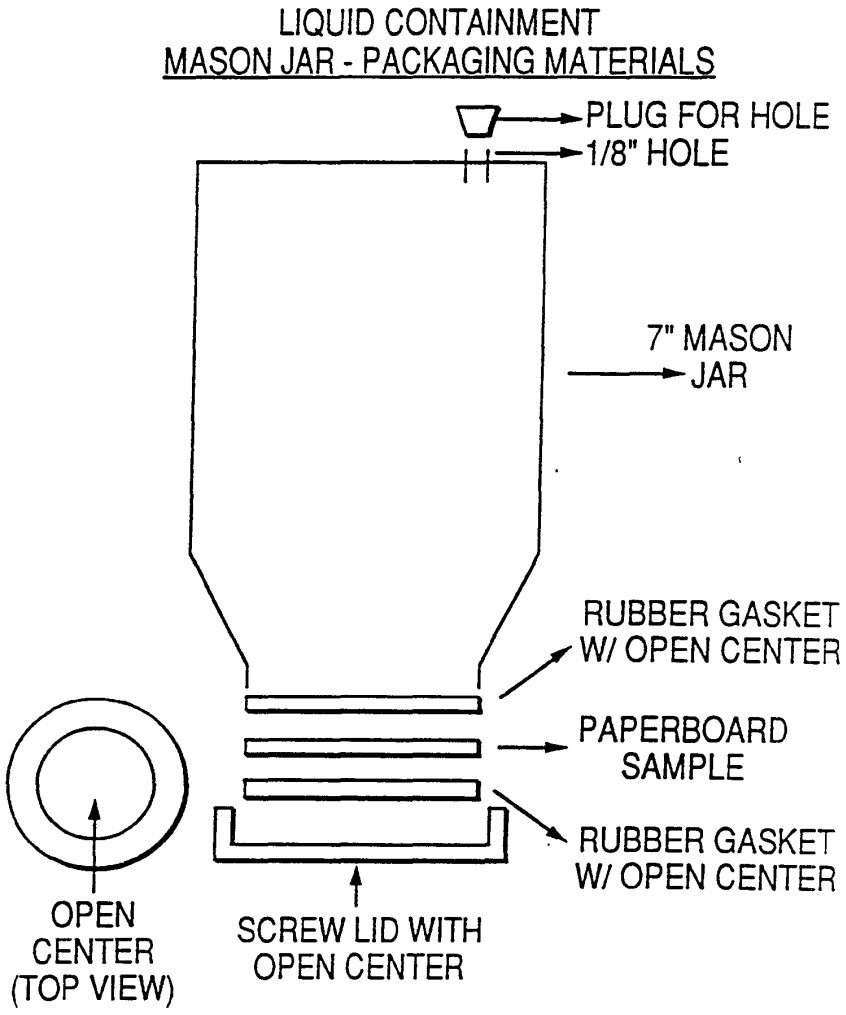

FIG. 12






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FIG. 13






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(54) Titre : PROCEDE DE PREPARATION DE FILMS ET DE REVETEMENTS
(54) Title: PROCESS FOR PREPARING FILMS AND COATINGS

(57) Abrégé/Abstract:
Extrusion films and coatings are prepared by applying a polyhydroxyalkanoate (PHA) to a surface which is in the range from 20 °C above to 20 °C below the optimum crystallisation temperature of the PHA. A PHA of high melt flow index is preferred.



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*With international search report.*

(54) Title: PROCESS FOR PREPARING FILMS AND COATINGS

(57) Abstract

Extrusion films and coatings are prepared by applying a polyhydroxyalkanoate (PHA) to a surface which is in the range from 20 °C above to 20 °C below the optimum crystallisation temperature of the PHA. A PHA of high melt flow index is preferred.

PROCESS FOR PREPARING FILMS AND COATINGS

This invention relates to a process of preparation of polymer films and polymer coatings on substrates, to the use of certain polymer compositions for the preparation of such films and coated substrates and to certain polymer compositions. In particular the invention relates to the use of polyhydroxy-alkanoate polyesters in such method and certain compositions thereof.

Films of polymers have many uses. Free standing films of plastics materials have innumerable industrial and consumer applications. Supported films, for example, coated paper, are also widely useful, particularly for imparting the qualities of moisture resistance and heat-sealability to the coated support.

In principle, films can be prepared from polymer either by using a preparation of molten polymer or by the use of a solution of polymer in a suitable solvent. In the latter case, it is clearly necessary to match a polymer with a suitable solvent for it; for polyhydroxyalkanoate polymers, which have the merit of being biodegradable, a problem exists in that the suitable solvents are generally chlorinated and therefore environmentally detrimental. Attention has therefore diverted to attempting to prepare films of these biodegradable, and hence environmentally friendly, polymers from molten preparations of the polymer; and it is to this area that the present invention is directed.

Extrusion coating of polymer films from molten polymer has been developed for a number of plastics, in

particular low density polyethylene. The standard procedure is for molten polyethylene to be extrusion coated onto a chilled roller, known in the art as a chill-roll. Low density polyethylene crystallises very quickly, and at reasonably low temperatures, so that it is adequately crystalline before it is drawn off the chill-roll, even when the roll is operating at very high line speeds, such as 700m/min. Polyhydroxyalkanoate polymers crystallise much more slowly than low density polyethylene at typical chill-roll temperatures.

The process of polyhydroxyalkanoate crystallisation from the molten state involves growth of spherulites, which are spherical regions of crystallised material around a nucleus. Such a nucleation site may occur in the pure polymer or can be artificially introduced by the use of a nucleating agent. The optimum temperature for creating nucleating sites is considerably lower than the optimum temperature for growth of the spherulites. However the optimum temperature for crystallisation is a combination of the two parameters and usually falls between the two parameters.

It has now been found that it is possible to adapt a chill-roll process for the preparation of a polyhydroxy-alkanoate film if the film formation is allowed to take place on the roll at a relatively high temperature compared to conventional extrusion coating processes, so as to improve or optimise crystallisation. The use of a high temperature chill roll allows relatively high line speeds and particularly high line speeds can be achieved using polyhydroxyalkanoate polymer with a high melt flow

index (MFI).

Thus, according to a first aspect of the present invention, there is provided a process for the preparation of extruded film or extrusion coating of a polyhydroxyalkanoate polymer, the process comprising applying a layer of molten polyhydroxyalkanoate to a surface which is at a temperature in the range from 20°C above to 20°C below the optimum crystallisation temperature of the polymer, so as to form a film or coating.

Crystallisation temperature range is dependent on the co-polymer content and various additives, primarily the nucleating agent.

The molten PHA preferably has a MFI of 12 or greater, especially 18 to 35.

Therefore, in a further embodiment of the present invention there is provided a process for the preparation of extruded film or an extrusion coating of a polyhydroxyalkanoate polymer, the process comprising applying a layer of molten polyhydroxyalkanoate having a melt flow index of 12 or greater to a surface which is at a temperature in the range from 20°C above to 20°C below the optimum crystallisation temperature of the polymer, so as to form a film or coating. The melt flow index may be determined according to the standard ASTM-D1238-906.

The present invention enables the film or coating formation to be carried out in a single stage process and allows much higher line speeds to be achieved than were previously possible by a single stage process.

The invention may be carried out with stereo-regular

PHAs, which may be produced by biological processes.

The polymer is especially one which is capable of a relatively high level of crystallinity, for example over 30%, especially 50-90%. Suitably it is or includes at least one biologically produced polyhydroxyalkanoate (PHA) having units of formula I:

$$- O - C_m H_n - CO - \qquad I$$

where m is in the range 1-13 and n is 2m or (when m is at least 2) 2m-2. Typically $C_m H_n$ contains 2-5 carbon atoms in the polymer chain and the remainder (if any) in a side chain. In very suitable polyesters m is 3 or 4, n is 2m and especially there are units with m = 3 and m = 4 copolymerised together with respectively a $C_1$ and $C_2$ side chain on the carbon next to oxygen. Particular polyesters contain a preponderance of m = 3 units, especially with at least 70 mol % of such units, the balance being units in which m = 4. The molecular weight of the polymer is for example over 50000, particularly over 100000, especially over 300000, up to, e.g. $2 \times 10^6$.

Polyester containing only m = 3 units is PHB, polyester containing m = 3 and m = 4 units is polyhydroxy-butyrate-co-valerate (PHBV). The polyester can also be a blend of two or more PHAs differing in the value of m. A particular example contains :

(a) polymer consisting essentially of Formula I units in which

2-5 mol % of units have m = 4, the rest m = 3; and

(b) polymer consisting essentially of Formula I units in which

5-30 mol % of units have m = 4, the rest m = 3.

The proportions of the polymers in such a blend are preferably such as give an average m = 4 content in the range 4-18 mol %.

The polyhydroxyalkanoate can be a fermentation product, especially of a microbiological process in which a microorganism lays down polyhydroxyalkanoate during normal growth or is caused to do so by cultivation in the absence of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have had the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by a eukariote, to effect the microbiological process.

Examples of suitable microbiological processes are the following:

for Formula I material with m = 3 or m = partly 3, partly 4: EP-A-69497 (Alcaligenes eutrophus);

for Formula I materials with m = 3:

US 4101533 (A. eutrophus), EP-A-144017 (A. latus);

for Formula I material with m = 7-13:

EP-A-0392687 (various Pseudomonas).

In such processes the polymer can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be decomposed using an aqueous route leaving microscopic particles of polymer. For specialised end uses the cellular protein may be partly or wholly allowed to remain with the polymer, but preferably subjected to cell breakage.

Alternately the PHA may be synthesised by chemical

processes known in the art. PHB can be prepared according to Bloembergen, S. and Holden, D. A., Macromolecules. 1989, Vol 22, p1656-1663. PHBV can be prepared according to Bloembergen, Holden, Bluhm, Hamer and Marchessault, Macromolecules. 1989, Vol 22, p1663-1669.

The invention is applicable also to synthetic polymers which are capable of crystallisation, especially:

a polyester, for example head-to-tail polyester or (preferably) substantially stoichiometric head-to-head tail-to-tail polyester;

b polyester having only alcohol or phenol reactivity or only acyl reactivity;

c other polymers, such a polyamides, having potential acylatable and or esterifiable groups.

Such polymers may be used alone or with one or more microbiologically derived polymers as described above. Examples of suitable synthetic polymers are synthetic polyhydroxyalkanoates, polylactides and copolymer of succinic acid and butylene glycol.

In or with the polymer there may be other materials present, in particular one or more plasticisers may be present. The ratio of plasticiser to polymer depends on the intended use of the composition. The range 2-40 phr w/w includes most of the likely uses. For making effectively rigid but not brittle articles the range 5-20 especially 6-12, phr w/w is generally suitable.

Any of the known plasticisers for these polymers are suitable and any plasticisers which are found to

plasticise these polymers subsequent to this invention would be suitable for use herein. Examples of suitable plasticisers are:

(a) high boiling esters of polybasic acids, such as phthalates, isophthalates, citrates, fumarates, glutamate, phosphates or phosphites. The esterified radicals may be for example $C_1$-$C_{12}$ alkyl, aryl or aralkyl. Particular examples are dioctyl-, dibeptyl- and dirindecyl- phthalates and dialkylalkylene oxide glutamate (Plasthall™ 7050);

(b) high boiling esters of polyhydric alcohols, especially glycols, polyglycols and glycerol. The acid derived radicals of the ester typically contains 2-10 carbon atoms. Examples are triacetin, diacetin and glyceryl dibenzoate;

(c) aromatic sulphonamides such as paratoluene sulphonamide.

A particularly preferred plasticiser is a doubly esterified hydroxycarboxylic acid having at least 3 ester groups in its molecule. "Doubly esterified" means that at least some of the hydroxy groups of the hydroxycarboxylic acid are esterified with a carboxylic acid and at least some of the carboxy groups thereof are esterified with an alcohol or phenol. Preferably at least the hydroxycarboxylic acid from which the ester is derived is aliphatic or cycloaliphatic. Its backbone structure (that is, apart from carboxy groups) preferably contains 2-6 carbon atoms. It contains preferably 2-4 carboxy groups and 1-3 hydroxy groups; and preferably the number of carboxy groups exceeds the number of hydroxy

groups. An example of such a plasticiser is Estaflex™ (acetyltri-n-butyl citrate).

In the process of the invention, the film is formed by applying the layer of the molten polyhydroxyalkanoate polymer to a surface. This application can be achieved by melt extrusion through an appropriately configured melt extrusion die. The configuration of the die is not believed to be particularly critical, and the precedents set in low density polyethylene melt extrusion methodology can be followed or readily adapted by those skilled in the art. However, when using high MFI polyester the die gap is preferably between from 0.1mm to 0.5mm and especially 0.1mm to 0.3mm

Molten polyhydroxyalkanoate may be co-extruded with one or more other polymers, which may have additional useful functionality (for example, by functioning as adhesives or barrier layers, for example). Generally and preferably the polyhydroxyalkanoate will be the layer which comes into contact with the surface of the chill-roll.

By means of the invention, films may be formed onto a substrate, which thereby becomes extrusion coated. The substrate may be any suitable material, such as paper, board or fabric, which may be knitted, woven or even non-woven. In the case of a non-woven fabric, the melt may penetrate into the non-woven structure, following the contours of the fabric. The substrate could also be a film of a second polymer. The second polymer should be a compatible polymer if a multilayer film is required. Alternatively, the second polymer should be non-

compatible if it is to be stripped from the first; this may leave the polyhydroxyalkanoate film with qualities superior to a comparable cast film.

A substrate may, prior to being coated, be pre-treated for example, by a corona treater. In practice, any suitable pre-treatment can be used if pre-treatment is required at all.

The invention is also suitable for preparing cast films, in which the polyhydroxyalkanoate film is not supported by a substrate. The film may be cast either onto a roller, as in certain chill-roll processes known from polyethylene casting, or the invention may use an adaption of such a process, for example, using an endless belt instead of a roller. The cast film may then be stretched, if required, before or while heating of the film takes place.

The temperature of the chill-roll or other surface on which the polymer is cast may be controlled by any suitable means. Suitable direct means include gas burners and electrical heating. A heat transfer fluid such as water or oil may, when appropriately remotely heated, be used in an indirect heating system.

The temperature of the surface used in the invention will depend on the optimal crystallisation temperature of the polymer from which film is being formed, which in turn varies with the polymer compositions. These crystallisation temperatures for polymers suitable for use in the invention can readily be determined by those skilled in the art. Typically, optimal crystallisation temperatures of suitable polymers will be in the range

50°C to 70°C.

A method of determining the optimal crystallisation temperature of the polymer is by Differential Scanning Calorimetry (DSC). In this method a Perkin Elmer DSC-7 is operated under programmed heating control from 20 to 200°C at 20°C $min^{-1}$ to measure melting behaviour. Crystallisation behaviour is monitored by cooling from 200 to 20°C at 20°C $min^{-1}$. From these measurements the melting peak temperature ($T_{m\ peak}$) and the crystallisation peak temperature ($T_{cryst}$) and enthalpies of fusion and crystallisation $\Delta H_{fus}$ and $\Delta H_{cryst}$ are determined.

At the temperature of the chill-roll or other surface used for film formation in the invention, crystallisation will occur at the temperatures used. This will enable higher line speeds to be used.

The crystallisation temperature may vary from polymer to polymer. In a polyhydroxybutyrate/valerate copolymer, it may vary with hydroxyvalerate content.

It is preferable in the present invention to use a polymer of high MFI, preferably 12 or greater, especially 18 to 35. The MFI can be measured by standard methods known in the art. The method used herein is ASTM - D1238-90b.

It is possible to raise the MFI of a polymer by different methods. For example, it is possible to obtain high MFI polymer by adding one or more plastisicers. In the present invention it is preferred to heat treat the polymer one or more times to degrade the average molecular weight (Mw). Most suitably the polymer produced by this method has a weight average Mw of

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350,000, and preferably 300,000 or below. Two useful methods to degrade the polymer are by extrusion compounding or by taking polymer and degrading with a basic solution, e.g. ammonium hydroxide.

The presence of a nucleating agent is often preferable in the polymer composition. Examples of conventional nucleating agents (to which the invention is no limited) include boron nitride (EP-A-0291024), ammonium chloride (WO-A-9919759) and DZB/ZnSt (EP-A-0400855). The amount of nucleating agent if present will generally be less than or equal to one part per hundred resin (phr) if only because of the wasted cost of adding excess nucleating agent. The lower limit of nucleating agent present is effectively 0 phr, which is to say that its presence is optional.

Another optional ingredient in the polymer composition is a release agent. Conventional release agents may be used, but the invention is not in any way restricted to the use of release agents which are known to date.

The polymer composition may contain any of the usual polymer processing additives, for example particulate fillers, reinforcing fibres and pigments.

However it is not usual to have these present in extrusion coating grades as it can affect the stability of the melt during draw-down from the die.

Films, whether coated on a web or free-standing, of various thicknesses can be produced by means of the invention. In particular, supported films (i.e. coatings), of from 1 to 100μm, and typically from 5 to

50μm, may be produced, and free standing films of from 5 to 150μm and typically from 10 to 100μm. It is also possible to use this process to make thick films greater than 150μm. It should be noted that the thicker the film the greater the heat transfer required to crystallise the coating therefore, thicker films often require slower lines speeds to be used with a heated chill roll.

The invention may be used to produce polyhydroxyalkanoate films at higher line speeds than has hitherto been possible in a single stage process. For example, line speeds of up to 300m/min, typically 50 to 200m/min are envisaged for extrusion coating. For cast film production line speeds up to 100m/min and typically 10 to 50m/min are envisaged. For thick film production line speeds up from 4 to 30m/min are envisaged.

According to a further aspect of the invention there is provided film and coated substrates produced by the process as defined herein.

The invention will now be illustrated with the following Examples.

EXAMPLE 1

A formulation of polyhydroxybutyrate/valerate copolymer was prepared having a hydroxyvalerate content of 5 mol % and 1 phr boron nitride nucleating agent. The granules had a molecular weight of 284,000 and MFI of 17 as measured by ASTM method no. 1238-90b, 2.16kg load at 180°C.

Granules of the formulation were fed into an extruder with a 40mm diameter screw. The screw was operated at a speed of 30-70 rpm. The extruder fed into

a 20cm wide die. The temperature of the melt was from 170 to 197°C as measured by thermocouples in the adaptor. The molten polymer was extruded into the nip between a first nip-roll and the chill-roll. A gloss chill-roll was used. The chill-roll was held at a temperature of 60°C; the die-gap was set to 0.2mm; the air gap between the die and the nip was set to about 10 cm. The polymer was coated on to paper (38g/m$^2$ or 80g/m$^2$) and board (200g/m$^2$), at line speeds of 55 to 100 m/min without the polymer exhibiting instability during draw-down of the melt.

The results for paper are given in Table 1.

Table 1

| Die Gap (mm) | Screw speed | line-speed |
|---|---|---|
| 0.5 | 30 | 30-35 |
| 0.5 | 50 | 35-40 |
| 0.5 | 70 | 43 |
| 0.2 | 30 | 55-60 |
| 0.2 | 70 | 85 |

Various coat weights were produced depending on the screw speed, die-gap and the line speed. The coating was satisfactory in its appearance and ran smoothly through to the wind-up. The coated paper and board could be unwound without any difficulties.

EXAMPLE 2

Example 1 was repeated using a formulation of polyhydroxy-butyrate/valerate copolymer was prepared

having a hydroxyvalerate content of 12 mol % and 1 phr boron nitride nucleating agent. The formulation was coated onto paper (40g/m$^2$). The die gap was 0.3mm. The die temperature was 190°C. The screw speed was varied from 20 to 80 rpm.

The results are presented in Table 2.

Table 2

| | line speeds (m/min) | | | |
|---|---|---|---|---|
| MFI | 20 (rpm) | 40 (rpm) | 60 (rpm) | 80 (rpm) |
| 3-4 | 30 | 35 | 35 | - |
| 24.8 | 70 | 84 | - | 112 |
| 18 | 60 | 81 | - | 112 |
| 24.8 | 86 | 104 | - | 110 |

It can be seen from the results that at low MFI the line speeds remain relatively low despite raising the screw speed. At each screw speed the high MFI materials gave much superior line speeds.



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CLAIMS:

1. A process for the preparation of extruded film or extrusion coating of a composition comprising a polyhydroxyalkanoate, the process comprising applying a molten layer of the composition to a surface which is at a temperature in the range from 20°C above to 20°C below the optimum crystallisation temperature of the polymer, so as to form a film or coating.

2. A process as claimed in claim 1, wherein the composition has a melt flow index of 12 or greater.

3. A process as claimed in claim 1 or 2, wherein the polymer has a weight average molecular weight of 350,000 or below.

4. A process as claimed in any one of claims 1 to 3, wherein the polymer is capable of over 30% crystallinity.

5. A process as claimed in any one of claims 1 to 4, wherein the polymer comprises at least one polyhydroxyalkanoate having units of general formula:

$$- O - C_mH_n - CO$$

in which m is 1 to 13 and n is 2m or, if m is at least 2, 2m-2.

6. A process as claimed in any one of claims 1 to 5, wherein the polymer is a polyhydroxybutyrate.

7. A process as claimed in any one of claims 1 to 5, wherein the polymer is a polyhydroxybutyrate-co-valerate comprising at least 70% hydroxybutyrate residues, the balance being hydroxyvalerate residues.

8. A process as claimed in any one of claims 1 to 7, wherein the crystallisation temperature is 35 to 85°C.

9. A process as claimed in claim 8, wherein the crystallisation temperature is 50 to 70°C.

10. A process as claimed in any one of claims 1 to 9, wherein nucleation is induced by a nucleating agent.

11. A process as claimed in claim 10, wherein the nucleating agent is boron nitride.

12. A process as claimed in any one of claims 1 to 11, wherein the polymer is stereo-regular.

13. A process as claimed in any one of claims 1 to 12, wherein the polymer is a biologically produced polyhydroxyalkanoate.

14. A process as claimed in any one of claims 1 to 13, wherein the molten layer of the composition is applied to the surface by melt extrusion through a die with a die gap of 0.1 to 0.5 mm.

15. A process as claimed in any one of claims 1 to 14, wherein the surface is that of a chill roll.

16. A process as claimed in any one of claims 1 to 15, wherein the composition contacts the surface directly.

17. A process as claimed in any one of claims 1 to 16, wherein the composition is coated onto paper or board.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS

# PATENT ABSTRACTS OF JAPAN

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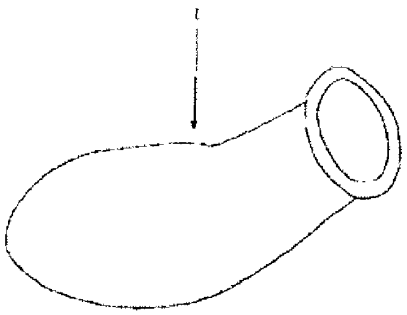
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## (54) UNDERGROUND DECOMPOSABLE EXCRETE VESSEL

(57)Abstract:
PROBLEM TO BE SOLVED: To enable an excrete vessel to be decomposed when buried underground to prolong the life of an administrative disposition land and to prevent pollution or destroy of natural environment, by forming the vessel by heating and melting a composition made by mixing respective quantity of vegetable residue powder, polyolefin based resin and/or biodegradable resin, and an additive.
SOLUTION: This underground decomposable excrete vessel, for instance a urine glass main body 1, is formed by heating and melting a composition made by mixing 20-80 wt.% of vegetable residue powder, 20-30 wt.% of polyolefin based resin and/or biodegradable resin, and 0.1-50 wt.% of an additive. The vessel has characteristics to be decomposed by microorganisms, etc., and the decomposing speed is increased by decaying of the vegetable residue in the vessel by moisture, etc., to cause to leave only little quantity of polyolefin based resin and ores and they can be in a condition near soil. Consequently land filling can be relatively easier by using the vessel to prolong the life of a filling land. The heating value is relatively low in burning treatment to make generation of toxic gas and poisonous gas lower than tolerance limits.



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(54)【発明の名称】　地中分解性排泄物容器

(57)【要約】

【目的】　自然環境に寄与する簡単で安価な地中分解性排泄物容器を提供する。

【構成】　植物残滓物粉末２０～８０重量％とポリオレフィン系樹脂及び／又は生分解性樹脂２０～８０重量％と添加剤０．１～５０重量％とを所定の配割合にて混合して得られた組成物を加熱溶融して所定の成形金型、ダイス等により地中分解性排泄物容器を得る。



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【特許請求の範囲】

【請求項１】植物残滓物粉末２０～８０重量％とポリオレフィン系樹脂及び／又は生分解性樹脂２０～８０重量％と添加剤０．１～５０重量％を混合してなる組成物を加熱溶融して成形したことを特徴とする地中分解性排泄物容器。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、地中に埋め立てた場合、微生物等により分解されたり、容易に焼却処分できる、いわゆる自然環境の汚染乃至は破壊を防止できる地中分解性排泄物容器に関する。

【０００２】

【従来の技術】従来、排泄物容器はガラス製のものやプラスチックを成形したものが市場を大きく形成しているが、使用後の洗浄の手間や破損したりして不要になったときの廃棄処理時に問題がある。即ち地中に埋め立てても生分解性がなく容器は半永久的に残存し、焼却すると発熱量が大きく焼却炉を破損しやすいという欠点がある。また、高齢化社会に伴い看護する人員が不足している状況であり、洗浄に手間がかかっている。

【０００３】植物残滓である食品加工時に発生する残滓物や木粉、木屑等は一部飼料や肥料に利用されているに留まり、大部分は埋め立てや焼却により廃棄処理されており、他に付加価値のある製品への利用が望まれていた。

【０００４】

【発明が解決しようとする課題】本発明が解決しようとする課題は、従来の排泄物容器の使用後における洗浄の手間や廃棄の問題、更に植物残滓物の用途が限られていることであって、本発明は上記課題を解決した地中分解性排泄物容器を提供しようとするものである。

【０００５】

【課題を解決するための手段】課題を解決するため本発明では、植物残滓物粉末２０～８０重量％とポリオレフィン系樹脂及び／又は生分解性樹脂２０～８０重量％と添加剤０．１～５０重量％を混合してなる組成物を加熱溶融して成形することによって地中分解性排泄物容器を生産するようになっている。

【０００６】

【発明の実施の形態】本発明の実施の形態を以下に詳細に説明する。排泄物容器を製造するにあたって、まず植物残滓物粉末とポリオレフィン系樹脂及び／又は生分解性樹脂と添加剤とを所定の配合割合にて調整して混合する。次いで混合された原料を射出成形機、押し出し成形機等により加熱溶融させ、成形金型、ダイス等によって排泄物容器の形状に成形する。

【０００７】植物残滓物は、穀類、豆類、麦類、種実類等を食品加工する際に発生する残滓物や木を加工する際に発生する木粉、竹粉、木屑等の廃材を用いる。残滓物

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は、乾燥され粉末状であればよく、１種又は２種以上組み合わせた混合物であっても使用可能である。これらのものは１０メッシュ程度の粉末で使用することができるが、製品の求める物性値、混合する樹脂の種類等によって、更に細粒化してもよい。

【０００８】使用されるポリオレフィン系樹脂及び／又は生分解性樹脂の内、ポリオレフィン系樹脂は、ポリプロピレン、高密度ポリエチレン、低密度ポリエチレン、エチレン－酢酸ビニル共重合体、プロピレン共重合体等を用いる。生分解性樹脂は、ポリヒドロキシブチレートとバリレートの共重合体、セルロース、微生物多糖類等の微生物系の生分解性樹脂、ポリ乳酸、ポリカプロラクトン、脂肪族ポリエステル等の化学合成系の生分解性樹脂、澱粉を含有する天然高分子系の生分解性樹脂等を用いる。樹脂の形状は、粉末が好ましいが、ペレット状であってもよい。これらの樹脂は１種又は２種以上組み合わせて使用してもよい。また、特に生分解性樹脂を使用したものは、微生物等による分解速度が生分解性樹脂単独のものに比べて短時間に分解するので、更に使用後における廃棄処理が容易に行える。

【０００９】植物残滓物とポリオレフィン系樹脂及び／又は生分解性樹脂との配合比率は、製品に要求される物性値、混合する樹脂の種類等によって設定されるが、一般的には、強度を高める場合には、植物残滓物の量の比率を小さくする。植物残滓物の樹脂への添加量は、２０～８０重量％であり、好ましくは３０～７０重量％、更に好ましくは３０～６０重量％である。

【００１０】添加剤の種類は、カップリング剤、潤滑剤、界面活性剤、強化剤、酸化防止剤、流動加速剤、充填剤、増量剤、補助剤、消臭剤、脱臭剤、着色剤、顔料、染料及びこれらの混合物がある。カップリング剤の例としては、組成物全体重量の０．１～２０重量％、好ましくは、０．５～１０重量％の範囲の比率であり、例えば、シランカップリング剤、チタンカップリング剤、シリコーン等がある。潤滑剤の例としては、組成物全体重量の０．１～１０重量％、好ましくは０．１～５重量％の範囲の比率であり、例えばステアリン酸カルシウム、ステアリン酸亜鉛等がある。強化剤の例としては、組成物全体重量の０．１～５０重量％、好ましくは０．１～３０重量％の範囲の比率であり、例えば炭酸カルシウム、タルク、マイカ、クレー等がある。消臭剤、脱臭剤の例としては、組成物全体重量の１～５０重量％、好ましくは１～３０重量％の範囲の比率であり、例えば木炭、活性炭、ゼオライト等がある。

【００１１】地中分解性排泄物容器は微生物等により分解するという性質を備えている。排泄物容器中の植物残滓物が水分等で腐食することにより分解速度を早め、残存するのは、少量のポリオレフィン系樹脂と鉱石類のみだが、土に近い状態になり得る。従って、これにより排泄物容器の埋め立て処理が比較的容易に行え、埋め立て



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地の延命化につながる。また、焼却処分する場合は、比較的発熱量が小さく、焼却炉を傷めることが少なく、有害ガスや有毒ガス等の発生も許容値以下なので容易に焼却できる。

【００１２】

【実施例】以下において実施例を具体的に説明する。植物残渣物として、大豆殻５４重量％と使用される樹脂としてポリプロピレン４０重量％と潤滑剤としてステアリン酸カルシウム１重量％と消臭剤としてゼオライト５重量％とを混合して得られた組成物を射出成形機に供給して成形温度１５０℃－１６０℃－１６０℃－１７５℃で排泄物容器を製造した。得られた排泄物容器は、加工性、寸法安定性、帯電防止性に優れ、樹脂成形排泄物容器の代替材になり得るものであった。次にこの排泄物容器を地中に埋め、３ヶ月後に取り出したところ、重量で約２０％減少しており、排泄物容器は崩壊しやすいものであった。

【００１３】植物残渣物として、大豆殻５０重量％と使用される樹脂として生分解性樹脂としてポリ乳酸（島津製作所製、商品名ラクティ）３７重量％、脂肪族ポリエステル（昭和高分子製、商品名ビオノーレ）５重量％と消臭剤としてゼオライト３重量％、木炭５重量％とを混合して得られた組成物を射出成形機に供給成形温度８０

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℃－１４０℃－１４０℃－１５５℃で排泄物容器を製造した。得られた排泄物容器は、加工性、寸法安定性、帯電防止性に優れ、樹脂成形排泄物容器の代替材になり得るものであった。次にこの排泄物容器を地中に埋め、３ヶ月後に取り出したところ、重量で約７０％減少しており、排泄物容器は崩壊しやすいものであった。

【００１４】

【発明の効果】以上説明したように、本考案は使用後不要になったとき、容易に処理ができることで付加価値を高めることができる。即ち、地中に埋めると微生物等により分解し、行政処分地の延命化が図れ、焼却した場合の発熱量が低く焼却炉を傷めることも少なく、黒煙や有害ガスも発生せず、自然環境の汚染乃至は破壊を防止する。

【００１５】

【図面の簡単な説明】

【図１】本発明にかかる地中分解性排泄物容器の斜視図である。

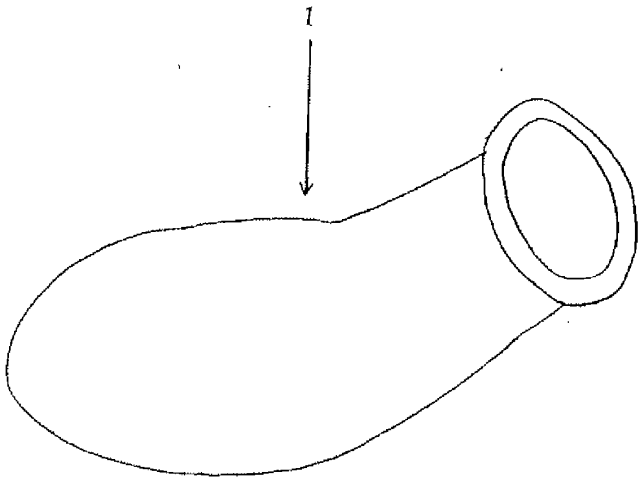
【図２】本発明にかかる地中分解性排泄物容器の斜視図である。

【符号の説明】

1　　尿器本体

2　　便器本体

【図１】

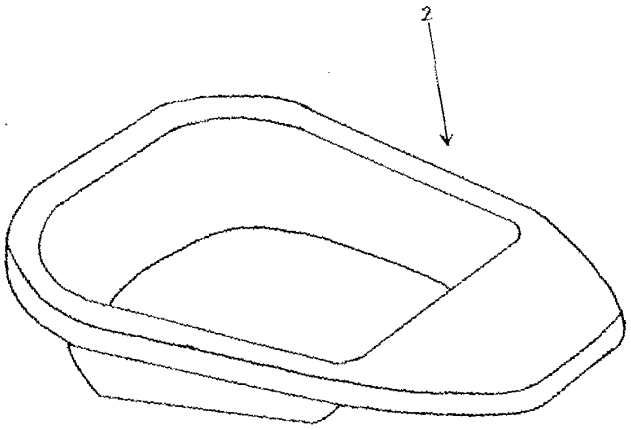





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(4)

【図2】






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**(54) Title:** COMPOSTIBLE LAMINATE

**(57) Abstract**

A composite laminate which comprises layers of a cellulose sheet, a polycaprolactone, polylactic acid and/or a poly 3- or 4-hydroxyalkanoic acid is compostible and has acceptable wet strength and resistance to cracking.

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**COMPOSTIBLE LAMINATE**

THIS INVENTION relates to compostible laminates.

Used packaging materials constitute a refuse disposal problem and it is desirable to be able to compost them. Also, in composting organic wastes, for example food or vegetation, it is convenient to transport the compostible material in a compostible container. Bags made of paper or other cellulosic material, for example cellulose film or boxes made of such materials, for example cardboard or the like may be used but are mechanically weak when wet.

This invention provides compostible laminates comprising cellulosic sheets, for example paper or board, of satisfactory strength which comprise substantially only compostible components and which comprise layers of a cellulose sheet, a polycaprolactone, a polylactic acid and/or a cellulose ester and a poly 3- or 4-hydroxy-alkanoic acid.

The invention preferably comprises a compostible laminate which comprises a cellulosic sheet directly coated on at least one surface with a layer of polycaprolactone, polylactic acid and/or a cellulose ester and a layer overlying the said directly coated layer of a poly 3 or 4-hydroxyalkanoic acid. We have found that laminates according to the invention have acceptable wet strength and resistance to cracking. Resistance to cracking is important if the paper or board is folded as any cracking along the fold will allow access to moisture and impairment of the wet strength along the fold.

The invention also comprises a compostible laminate as aforesaid in which the polyhydroxyalkanoic acid layer is covered with a readily removable sacrificial layer of optionally non-compostible polymer, for example polythene or polypropylene. The sacrificial layer is useful in improving the manufacture of the laminate, for example in preventing the sticking of the laminate to chill rolls in the course of manufacture. If desired it may be left in position to protect the laminate until it is to be used.

The added layers may be applied to the cellulosic sheet simultaneously using known techniques, for example by the use of a multi manifold co-extruder. Temperatures of 150 to 300°C and preferably 150 to 250°C are suitably used for co-extrusion and polymers with melting points below the extrusion temperature should be used. After application of the added layers the laminate is suitably cooled for example to a temperature of 40 to 70°C. This may be accomplished by contacting the laminate with a chill roller.

It is preferred that the total weight of the coating layers after stripping the sacrificial layer from the product should be about 5 to 40 grammes per square metre and is preferably 10-25 grammes per square metre. The ratio of the polyhydroxyalkanoic acid to the polycaprolactone, cellulose ester or polylactic acid layer may be 1:10 to 10:1 preferably 5:1 to 1:5 and more preferably 2:1 to 1:2 by weight

The polyhydroxyalkanoic acid may be a homo or co-polymer suitably of hydroxybutyric acid preferably together with hydroxyvaleric acid. Suitable polymers of

this type are described in our European Patents EP 52459 and EP 69497. The polyhydroxyalkanoic acid preferably has a molecular weight of 50,000 to 1 million and more preferably 100,000 to 800,000. The polylactic acid, cellulose ester or polycaprolactone preferably has a molecular weight of at least 40,000 for example 30,000 to 500,000.

The sacrificial layer may after it is stripped from the laminate be reused in the manufacturing process if it is a thermo-plastic.

A pilot line was used for the following work which comprises a roll of 110g/m$^2$ brown Kraft paper feeding the paper to a unit for corona discharge onto the paper, a support roller supporting the paper emerging from the corona discharge chamber, a die for extruding three layers of polymer onto the paper beyond the support roller, a chill roller and a nip roller for pressing the laminate of paper and polymer together against the chill roller and a wind-up roller for collecting the laminate.

The corona discharge was at a power of approximately 1.5 kw over a width of 350 mm, the paper being run through the discharge at a rate of 15 to 75 m per minute.

The die was fed by three extruders supplying polycaprolactone (a commercial product sold as "Tone" 767 by Union Carbide, estimated number average molecular weight 43,000 melt flow index of 30 at 190°C), a copolymer comprising 92% hydroxybutyric acid units and 8% hydroxyvaleric acid units in a D-configuration of estimated weight average molecular weight 480,000 sold under the trade name "BIOPOL" by ZENECA Limited and low

density polyethylene sold by Borealis as grade NCPE 1515, MFI 15 at 190°C. The die was a Cloeren vane flat die of width 350 mm with adjustable vanes and equipped with breaker plates and screen packs and using a CCABB configuration plug.

This arrangement enabled the polymers to be extruded onto the paper in the order paper/polycaprolactone/-"BIOPOL" polyhydroxyalkanoate/polyethylene in the desired thicknesses set by the outputs from each extruder.

The chill roller was maintained at a temperature of 60°C.

The line was operated under the conditions shown below. For comparison a single layer consisting of "BIOPOL" polymer was coated onto the paper using only one of the extruders under the conditions shown below. The "Barrel Zone" temperatures indicate the successive increases in temperature in the barrel zones of the extruders which feed adaptors of the extruders which adjust the temperature of the polymer as shown. The temperature of the die itself was set at 185°C.

**Single Layer Extrusion**

| Sample | Barrel Zones °C | | | Adaptor °C | Screw Speed rpm | Line speed m/min |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | | | |
| #1 | 150 | 175 | 185 | 185 | 40 | 30 |
| #2 | 150 | 175 | 185 | 185 | 40 | 20 |
| #3 | 150 | 175 | 185 | 185 | 40 | 25 |

3 Layer Co-Extrusion

| Sample | Barrel Zones °C | | | | Adap -tor °C | Screw speed rpm | Line speed m/min |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | | | |
| #9 | 150 | 175 | 185 | | 185 | 45 | 35 |
| | 150 | 170 | 180 | 185 | 185 | 20 | |
| | 150 | 170 | 180 | 185 | 185 | 90 | |
| #10 | 150 | 175 | 185 | | 185 | 32 | 35 |
| | 150 | 170 | 185 | 185 | 185 | 32 | |
| | 150 | 170 | 185 | 185 | 185 | 90 | |
| #20 | 150 | 175 | 185 | | 185 | 50 | 50 |
| | 150 | 175 | 180 | 185 | 185 | 50 | |
| | 170 | 190 | 195 | 200 | 205 | 200 | |
| #21 | 150 | 175 | 185 | | 185 | 50 | 75 |
| | 150 | 170 | 180 | 185 | 185 | 50 | |
| | 170 | 190 | 195 | 200 | 205 | 200 | |

The screw speeds in the preceding table are proportional to the approximate relative thickness of the layers.

The products were tested as follows:

Laminate from the wind-up roller was removed and any polyethylene layer stripped off. The coat weight (i.e. the total polymer remaining per square metre of laminate) was recorded.

Adhesion of the layers was tested by manual

stripping of the deposited polymer layers from the paper.

Cracking of the polymer layer was tested by folding the laminate over so that the polymer layer contacted the polymer layer, the direction of folding being transverse to the line processing direction or parallel to the line processing direction as the case may be, and also so that the paper layer contacted the paper layer in the transverse and parallel directions as aforesaid.

The integrity of the polymer coating after folding was tested by laying the laminate flat, applying coloured turpentine to the crease from the polymer side of the laminate and after 10 minutes measuring the proportion of the crease in which colouring on the paper side was observed. 10 cm lengths of crease were tested.

The results are reported as follows:

| Sample | Coat Weight $g/m^2$ | Adhesion Number | Turpentine (Line Direction) Substrate to Substrate (%) | Coating to Coating (%) | Turpentine (Traverse Direction) Substrate to Substrate (%) | Coating to Coating (%) |
|---|---|---|---|---|---|---|
| #1 | 15 | 0 | 60 | 80 | 90 | 50 |
| #3 | 20.5 | 0 | 20 | 70 | 50 | 50 |
| #2 | 28 | 0 | 0 | 0 | 0 | 0 |
| #21 | 12.1 | 5 | 5 | 0 | 5 | 1 |
| #20 | 14.4 | 5 | 1 | 3 | 5 | 1 |
| #10 | 18.6 | 3 | 1 | 0 | 5 | 0 |
| #9 | 21.0 | 2 | 1 | 0 | 5 | 0 |

#1, #2 and #3 all single layer extrusion coating

#21. #20 and #10 are all 3 layer co extrusions with equal "BIOPOL" Polymer to PCL layers

#9 is a 3 layer co extrusion with a 9/4 ratio of "BIOPOL" Polymer to PCL

PCL means polycaprolactone. Adhesion numbers are assessed as follows:



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| | |
|---|---|
| Adhesion 0 | Layers not bonded at all and both materials remain completely intact. |
| Adhesion 1 | Layers come apart easily and both materials remain completely intact. |
| Adhesion 2 | Some force needed to separate the layers and materials damaged slightly. |
| Adhesion 3 | More force needed to separate the layers and both materials damaged. |
| Adhesion 4 | Layers difficult to pull apart and both damaged almost totally. |
| Adhesion 5 | Layers impossible to pull apart, both tear immediately. |

CLAIMS

1 A laminate which comprises layers of a cellulosic sheet, a poly caprolactone, a polylactic acid and/or a cellulose ester and a poly 3- or 4-hydroxyalkanoic acid.

2 A laminate as claimed in Claim 1 in which the cellulosic sheet is paper or board.

3 A compostible laminate which comprises a cellulosic sheet directly coated on at least one surface with a layer of polycaprolactone, polylactic acid and/or a cellulose ester and a layer overlying the said directly coated layer of a poly 4- or 5- hydroxy-alkanoic acid.

4 A compostible laminate as claimed in any preceding claim in which the polyhydroxyalkanoic acid layer is covered with a readily removable sacrificial layer of optionally non-compostible polymer.

5 A laminate as claimed in Claim 4 in which the sacrificial layer is of polythene or polypropylene.

6 A laminate as claimed in any of Claims 1 to 5 in which the total weight of the layers other than the cellulosic sheet after stripping any sacrificial layer from the product is 4 to 40 grams per square metre.

7 A laminate as claimed in any preceding claim in which the ratio of the polyhydroxyalkanoic acid to polycaprolactone cellulose ester or polylactic acid is 1:10 to 10:1 by weight.

8 A laminate as claimed in any preceding claim in which the polyhydroxyalkanoic acid is a homo or