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Questions about this communication ?
Contact Customer Services at www.epo.org/contact

Tomkinson, Alexandra
Bailey Walsh & Co LLP
1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date
22.05.19

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1110 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Communication regarding the expiry of the time limit within which notice of opposition may be filed

You are hereby informed that on expiry of the nine-month time limit from the publication of the mention of the grant of European patent No. 2842423 no notice of opposition had reached the files.

The entry in the Register of European Patents will be automatically generated by the electronic data processing system.

For the Examining Division

Europäisches Patentamt • European Patent Office • Office européen des brevets

EPPU 02: 18.07.18 1110

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 001

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Contact Customer Services at www.epo.org/contact

Tomkinson, Alexandra
Bailey Walsh & Co LLP
1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date
30.07.18

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1110 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Transmission of the certificate for a European patent pursuant to Rule 74 EPC

The certificate for a European patent is herewith transmitted.

The European patent specification can be downloaded from the EPO publication server **https://data.epo.org/publication-server/** (see OJ EPO 2005, 126).

Note:
A corrected title page of the European patent specification will be published, if the bibliographic data have been changed after completion of the technical preparations.

For the Examining Division



Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
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Questions about this communication ?
Contact Customer Services at www.epo.org/contact

Tomkinson, Alexandra
Bailey Walsh & Co LLP
1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date
21.06.18

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1110 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Decision to grant a European patent pursuant to Article 97(1) EPC

Following examination of European patent application No. 14185786.2 a European patent with the title and the supporting documents indicated in the communication pursuant to Rule 71(3) EPC (EPO Form 2004C) or in the information (EPO Form 2004W, cf. Notice from the EPO dated 8 June 2015, OJ EPO 2015, A52) dated 16.03.18 is hereby granted in respect of the designated Contracting States.

Patent No. : 2842423
Date of filing : 24.03.11
Priority claimed : /

Designated Contracting States and Proprietor(s) : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Enviro Tech Chemical Services Inc.
500 Winmoore Way
Modesto, CA 95358/US

This decision will take effect on the date on which the European Patent Bulletin mentions the grant (Art. 97(3) EPC).

The mention of the grant will be published in European Patent Bulletin 18/29 of 18.07.18.

Examining Division

Lorenzo Varela M Sawicki M Bertrand F

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Registered letter
EPO Form 2006A 07.15 (14/06/18)

to EPO postal service: 15.06.18

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
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ANMERKUNG ZUR ENTSCHEIDUNG ÜBER DIE ERTEILUNG
EINES EUROPÄISCHEN PATENTS (EPA Form 2006)

1. **EPA Informationsbroschüre "Nationales Recht zum EPÜ"**
Diese Broschüre enthält nützliche Informationen zu den formalen Erfordernissen und den Handlungen, die vor den Patentbehörden der Vertragsstaaten vorzunehmen sind, um Rechte in diesen Staaten zu erlangen. Da diese Handlungen einem ständigen Wandel unterworfen sind, sollte immer nur die neueste Ausgabe der Broschüre benutzt werden. Nachträgliche Informationen werden im Amtsblatt veröffentlicht.

2. **Übersetzung der europäischen Patentschrift nach Artikel 65 (1) des Europäischen Patentübereinkommens**
Sie werden erneut darauf hingewiesen, dass bestimmte Vertragsstaaten nach Artikel 65 (1) EPÜ eine Übersetzung der europäischen Patentschrift verlangen; hierauf wird in der Mitteilung gemäß Regel 71 (5) EPÜ verwiesen. Die Nichteinreichung dieser Übersetzung kann zur Folge haben, dass das Patent in dem betreffenden Staat/in den betreffenden Staaten als von Anfang an nicht eingetreten gilt. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.

3. **Zahlung von Jahresgebühren für europäische Patente**
Nach Artikel 141 EPÜ können "nationale" Jahresgebühren für das europäische Patent für die Jahre erhoben werden, die an das Jahr anschließen, in dem der Hinweis auf die Erteilung des europäischen Patents im "Europäischen Patentblatt" bekanntgemacht wird. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.

NOTE RELATING TO THE DECISION TO GRANT A
EUROPEAN PATENT (EPO Form 2006)

1. **EPO Information Brochure "National law relating to the EPC"**
This brochure provides useful information regarding formal requirements and the steps to be taken before the patent authorities of the Contracting States in order to acquire rights in those states. Since the necessary steps are subject to change the latest edition of the brochure should always be used. Subsequent information is published in the Official Journal.

2. **Translation of the European patent application under Article 65(1) of the European Patent Convention**
Your attention is again drawn to the requirements regarding translation of the European patent specification laid down by a number of Contracting States under Article 65(1) EPC, to which reference is made in the communication under Rule 71(5) EPC. Failure to supply such translation(s) may result in the patent being deemed to be void "ab initio" in the State(s) in question. For further details you are recommended to consult the above-mentioned brochure.

3. **Payment of renewal fees for European patents**
Under Article 141 EPC "national" renewal fees in respect of a European patent may be imposed for the years which follow that in which the mention of the grant of the European patent is published in the "European Patent Bulletin". For further details you are recommended to consult the above-mentioned brochure.

REMARQUE RELATIVE A LA DECISION DE DELIVRANCE
D'UN BREVET EUROPEEN (OEB Form 2006)

1. **Brochure d'information de l'OEB "Droit national relatif à la CBE"**
Cette brochure fournit d'utiles renseignements sur les conditions de forme requises et sur les actes à accomplir auprès des offices de brevet des Etats contractants aux fins d'obtenir des droits dans les Etats contractants. Etant donné que les actes indispensables sont susceptibles de modifications, il serait bon de toujours consulter la dernière édition de la brochure. Toute information ultérieure est publiée au Journal Officiel.

2. **Traduction du fascicule du brevet européen en vertu de l'article 65(1) de la Convention sur le brevet européen**
Votre attention est de nouveau attirée sur l'obligation faite par certains Etats contractants, en vertu de l'article 65(1) CBE, de fournir une traduction du fascicule du brevet européen, à laquelle il est fait référence dans la notification établie conformément à la règle 71(5) CBE. Si la(les) traduction(s) n'est(ne sont) pas fournie(s), le brevet européen peut, dès l'origine, être réputé sans effet dans cet(ces) Etat(s). Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.

3. **Paiement des taxes annuelles pour le brevet européen**
Conformément à l'article 141 CBE des taxes annuelles "nationales" dues au titre du brevet européen peuvent être perçues pour les années suivant celle au cours de laquelle la mention de la délivrance du brevet européen est publiée au "Bulletin européen des brevets. Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 004

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GERMANY

Questions about this communication ?
Contact Customer Services at www.epo.org/contact

Tomkinson, Alexandra
Bailey Walsh & Co LLP
1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date
15.06.2018

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1110 / 2842423

Applicant/Proprietor
Enviro Tech Chemical Services Inc.

BRIEF COMMUNICATION

Subject:
- [X] Your letter of 07.06.2018
- [ ] Our telephone conversation of
- [ ] Communication of
- [ ]

Enclosure(s):
- [ ] Letter from the proprietor of the patent of
- [X] Copy (copies) form 2056
- [ ] Communication:

The data of the inventors have been recorded according to your request.

Please take note.

For the Legal Division

Europäisches Patentamt • European Patent Office • Office européen des brevets

☐ **Registered letter**

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 005

Europäisches Patentamt
European Patent Office
Office européen des brevets

Annex to EPO Form 2004, Communication pursuant to Rule 71(3) EPC

Bibliographical data of European patent application No. 14185786.2.

For the intended grant of the European patent, the bibliographic data are set out below, for information:

Title of invention:
- VERFAHREN ZUR ERZEUGUNG VON PERESSIGSÄURE DIREKT AM VERWENDUNGSORT
- METHOD FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE.
- PROCÉDÉ POUR LA GÉNÉRATION D'ACIDE PERACÉTIQUE SUR SITE AU NIVEAU DU POINT D'UTILISATION

Classification: A01N37/16, A01N25/00, A61K31/075, A61L9/00, A61L2/18, A61K31/327, A01P1/00

Date of filing: 24.03.11

Priority claimed: / /

Contracting States* for which fees have been paid: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Extension States* for which fees have been paid:

Validation States* for which fees have been paid:

Applicant(s) **:
Enviro Tech Chemical Services Inc.
500 Winmoore Way
Modesto, CA 95358/US

Inventor(s):
Harvey, Michael S.
500 Winmoore Way
Modesto, CA 95358
US

Howarth, Jonathan N.
3804 Viader Drive
Modesto, CA 95356
US

*) If the time limit for the payment of designation fees according to Rule 39(1) EPC has not yet expired and the applicant has not withdrawn any designation, **all Contracting States/Extension States/Validation States** are currently still deemed to be designated. See also Rule 71a(3) EPC and, if applicable, the above Note to users of the automatic debiting procedure.

**) If two or more applicants have designated different Contracting States, this is indicated here.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 006

Europäisches Patentamt
European Patent Office
Office européen des brevets

Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	6396644
Application number	EP14185786.2
Date of receipt	07 June 2018
Receiving Office	European Patent Office, The Hague
Your reference	AT-X11031DIV2-E
Applicant	All applicants as on file
Documents submitted	package-data.xml epf1038.pdf (2 p.) CLMSTRAN-DE-1.pdf\X11031DIV2-EP - German Translation of Claims.pdf (1 p.) ep-sfd-request.xml CLMSTRAN-FR-1.pdf\X11031DIV2-EP - French Translation of Claims.pdf (1 p.) IGRA-1.pdf\X11031DIV2-EP - Change of address of inventors.pdf (2 p.)
Submitted by	CN=David Corbyn 29824
Method of submission	Online
Date and time receipt generated	07 June 2018, 10:25 (CEST)
Message Digest	89:C7:79:24:4E:AC:C5:87:D3:F5:FD:E6:E3:C0:54:0F:82:9B:EA:5D

Correction by the EPO of errors in debit instructions filed by eOLF
Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 007

European Patent Office
Erhardstrasse 27
D-80298 Munich
Germany

Our ref.: AT-SAR-X11031DIV2-EP
Your ref.:
7 June 2018

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

I refer to the abovementioned patent application and further to the Communication under Rule 71(3) EPC dated 16th March 2018 and would you please update the addresses of the inventors to the following:-

Michael S Harvey
500 Winmoore Way
Modesto
CA 95358
USA

Jonathan N Howarth
3804 Viader Drive
Modesto
CA 95356
USA

Yours faithfully,
BAILEY WALSH & CO LLP

I look forward to receiving your confirmation that the Patents Register has been updated accordingly.

A. Tomkinson

REVENDICATIONS

1. Procédé pour la génération d'une solution hors d'équilibre d'acide péracétique, comprenant les étapes consistant à :

a. fournir de l'eau ;

b. introduire de la triacétine et du peroxyde d'hydrogène aqueux dans l'eau séparément, soit simultanément, soit séquentiellement, avec l'un quelconque d'entre eux en premier ;

c. mélanger la triacétine et le peroxyde d'hydrogène aqueux avec l'eau de manière à former un mélange ;

d. ajouter la source aqueuse d'un métal alcalin ou d'un hydroxyde de métal alcalino-terreux au mélange ; et

e. former un milieu de réaction comprenant une solution hors d'équilibre d'acide péracétique, caractérisé en ce que la source aqueuse du métal alcalin ou de l'hydroxyde de métal alcalino-terreux est de l'hydroxyde de sodium à 1,82 % à 7,28% en poids, et dans lequel le rapport molaire de l'hydroxyde de sodium au peroxyde d'hydrogène à la triacétine est de 4,2 : 3,8 : 1.

2. Procédé selon la revendication 1, comprenant par ailleurs le fait de laisser le milieu de réaction avoir un temps de réaction de 30 secondes à cinq minutes.

Patentansprüche

1. Verfahren zum Erzeugen einer Nichtgleichgewichtslösung aus Peroxyessigsäure, umfassend:

a. Bereitstellen von Wasser;

b. Zuführen von Triacetin und wässrigem Wasserstoffperoxid, entweder gleichzeitig oder nacheinander, mit einem beliebigen zuerst, zu dem Wasser;

c. Vermischen des Triacetins und des wässrigen Wasserstoffperoxids mit dem Wasser zu einem Gemisch;

d. Zugeben einer wässrigen Quelle eines Alkalimetall- oder Erdalkalimetallhydroxids zu dem Gemisch und

e. Bilden eines Reaktionsmediums, umfassend eine Nichtgleichgewichtslösung aus Peroxyessigsäure, dadurch gekennzeichnet, dass die wässrige Quelle des Alkalimetall- oder Erdalkalimetallhydroxids Natriumhydroxid bei 1,82 Gew.-% bis 7,28 Gew.-% ist und wobei das Molverhältnis des Natriumhydroxids zum Wasserstoffperoxid zum Triacetin 4,2:3,8;1 ist.

2. Verfahren nach Anspruch 1, ferner umfassend das Zulassen einer Reaktionszeit von 30 Sekunden bis fünf Minuten für das Reaktionsmedium.

Europäisches Patentamt
European Patent Office
Office européen des brevets

Letter accompanying subsequently filed items

Representative:

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Bailey Walsh & Co LLP
1 York Place
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United Kingdom

Phone: 00 44 113 243 3824
Fax: 00 44 113 244 5699
E-mail: mail@bailey-walsh.com

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2280 HV Rijswijk
Netherlands
Tel. +31(0)70 340-2040 | Fax -3016

10958 Berlin
Germany
Tel. +49(0)30 25901-0 | Fax -840

The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number	14185786.2
Applicant's or representative's reference	AT-X11031DIV2-E

	Description of document	Original file name	Assigned file name
1	French translations of the claims	X11031DIV2-EP - French Translation of Claims.pdf	CLMSTRAN-FR-1.pdf
2	German translations of the claims	X11031DIV2-EP - German Translation of Claims.pdf	CLMSTRAN-DE-1.pdf
3	Reply to the communication under rule 71(3) EPC	X11031DIV2-EP - Change of address of inventors.pdf	IGRA-1.pdf

	Fees	Factor applied	Fee schedule	Amount to be paid
15-1	007 Fee for grant, including fee for publication of the European patent specification (R71(3))	1	925.00	925.00
	Total:		**EUR**	**925.00**

	Payment	
1	Method of payment	Debit from deposit account
	Currency:	EUR
	The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.	
	Deposit account number:	28050202
	Account holder:	Bailey Walsh & Co LLP
2	Refund/Reimburserment	
	Reimbursement (if any) to be made to EPO deposit account:	28050202
	Account holder:	Bailey Walsh & Co LLP

Signatures

Place: **Leeds**

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 012

Date:	07 June 2018
Signed by:	David Corbyn 29824
Representative name:	Alexandra Tomkinson
Capacity:	(Representative)

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 013

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Annex to EPO Form 2004, Communication pursuant to Rule 71(3) EPC

Bibliographical data of European patent application No. 14 185 786.2

For the intended grant of the European patent, the bibliographical data are set out below, for information:

Title of invention:	- VERFAHREN ZUR ERZEUGUNG VON PERESSIGSÄURE DIREKT AM VERWENDUNGSORT - METHOD FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE. - PROCÉDÉ POUR LA GÉNÉRATION D'ACIDE PERACÉTIQUE SUR SITE AU NIVEAU DU POINT D'UTILISATION
Classification:	INV. A01N37/16 A01N25/00 A61K31/075 A61L9/00 A61L2/18 A61K31/327 A01P1/00
Date of filing:	24.03.2011
Priority claimed:	
Contracting States* for which fees have been paid:	AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Extension States* for which fees have been paid:	
Validation States* for which fees have been paid:	
Applicant(s):**	Enviro Tech Chemical Services Inc. 500 Winmoore Way Modesto, CA 95358 US
Inventor(s):	Harvey, Michael .S. 712, Faust Road Modesto, CA California CA95358 US Howarth, Jonathan . N. 3804 Vader Drive Modesto, CA 95356 US

*) If the time limit for the payment of designation fees according to Rule 39(1) EPC has not yet expired and the applicant has not withdrawn any designation, **all Contracting**

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 014

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States/Extension States/Validation States are currently still deemed to be designated.
See also Rule 71a(3) EPC and, if applicable, the above Note to users of the automatic debiting procedure.

**) If two or more applicants have designated different Contracting States, this is indicated here.

Petitioner's Exhibit 1022
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Formalities Officer
Name: Flanter, Gerda
Tel: +49 89 2399 - 7024
or call
+31 (0)70 340 45 00

Application No.	Ref.	Date
14 185 786.2 - 1110	AT-BF-G49415	16.03.2018
Applicant Enviro Tech Chemical Services Inc.		

Communication under Rule 71(3) EPC

1. Intention to grant

You are informed that the examining division intends to grant a European patent on the basis of the above application, with the text and drawings and the related bibliographic data as indicated below.

A copy of the relevant documents is enclosed.

1.1 In the text for the Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Description, Pages

1-24	received on	07-09-2015	with letter of	07-09-2015

Claims, Numbers

1, 2	received on	22-01-2018	with letter of	22-01-2018

Drawings, Sheets

1/1 as originally filed

With the following amendments to the above-mentioned documents proposed by the division

Description, Pages 1, 3, 7, 8, 12-19, 22

Comments

description adapted to amended claims, and vague and ambiguous terms deleted (Art. 84 EPC)

Registered letter
EPO Form 2004C 12.17CXP

SI units additionally given (Rule 49(10) EPC)

1.2 Bibliographic data

The title of the invention in the three official languages of the European Patent Office, the international patent classification, the designated contracting states, the registered name(s) of the applicant(s) and the other bibliographic data are shown on **EPO Form 2056** (enclosed).

2. Invitation

You are invited, **within a non-extendable period of four months** of notification of this communication,

2.1 to EITHER approve the text communicated above and verify the bibliographic data (Rule 71(5) EPC)

(1) by filing a translation of the claim(s) in the other two official languages of the EPO

	Fee code	EUR
(2a) by paying the fee for grant including the fee for publication:	**007**	925.00
minus any amount already paid (Rule 71a(5) EPC):		0.00
Total amount:		925.00
(3) by paying additional claims fees under Rule 71(4) EPC; number of claims fees payable: 0	**016**	0.00
minus any amount already paid (Rule 71a(5) EPC):		0.00
Total amount:		0.00

Important: If the translations of the claims and fees have already been filed and paid respectively in reply to a previous communication under Rule 71(3) EPC, e.g. in the case of resumption of examination after approval (see Guidelines C-V, 6), **agreement as to the text to be granted** (Rule 71a(1) EPC) must be expressed within the same time limit (e.g. by approving the text and verifying the bibliographic data, by confirming that grant proceedings can go ahead with the documents on file and/or by stating which translations of the claims already on file are to be used).

Note 1: See "Notes concerning fee payments" below.
Note 2: Any overpaid "minus" amounts will be refunded when the decision to grant (EPO Form 2006A) has been issued.
Note 3: For the calculation of the grant fee under Article 2(2), No. 7, RFees (old fee structure), the number of pages is determined on the basis of a clean copy of the application documents, in which text deleted as a result of any amendments by the examining division is not shown. Such clean copy is made available via on-line file inspection only.

2.2 OR, in the case of disapproval, to request reasoned amendments or corrections to the text communicated above or keep to the latest text submitted by you (Rule 71(6) EPC).

In this case the translations of the claims and fee payments mentioned under point 2.1 above are NOT due.

The terms "amendment(s)" and "correction(s)" refer only to amendments or corrections of the application documents and not of other documents (e.g. bibliographic data, the designation of the inventor, etc.).

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If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the examining division requesting that you correct this deficiency (Rule 137(4) EPC).

2.3 Bibliographic data

Where you request a change or correction of bibliographic data in response to the Rule 71(3) communication, this will **not** cause the sending of a further communication under Rule 71(3) EPC. You will still have to pay the fees and file translations in reply to the Rule 71(3) communication in the case of 2.1 above, unless you also file a reasoned request for amendments or corrections in response to the Rule 71(3) communication (see case 2.2 above).

3. Loss of rights

If neither of the two possible actions above (see points 2.1 or 2.2) is performed in due time, the European patent application will be deemed to be withdrawn (Rule 71(7) EPC).

4. Further procedure

4.1 In the case of point 2.1 above

4.1.1 The decision to grant the European patent will be issued, and the **mention of the grant** of the patent will be published in the European Patent Bulletin, if the requirements concerning the translation of the claims and the payment of all fees are fulfilled and there is agreement as to the text to be granted (Rule 71a(1) EPC).

Note on payment of the renewal fee:
If a renewal fee becomes due before the next possible date for publication of the mention of the grant of the European patent, publication will be effected only after the renewal fee and any additional fee have been paid (Rule 71a(4) EPC).

Under Article 86(2) EPC, the obligation to pay renewal fees to the European Patent Office terminates with the payment of the renewal fee due in respect of the year in which the mention of the grant of the European patent is published.

Note on payment of the designation fee(s):
If the designation fee(s) become(s) due after the communication under Rule 71(3) EPC, the mention of the grant of the European patent will not be published until these fees have been paid (Rule 71a(3) EPC).

4.1.2 After publication, the **European patent specification** can be downloaded free of charge from the EPO publication server https://data.epo.org/publication-server.

4.1.3 Filing of translations in the contracting states

As regards translation requirements prescribed by the contracting states under Article 65(1) EPC, please consult the website of the European Patent Office
www.epo.org ➞Law & practice ➞Legal texts, National law relating to the EPC
www.epo.org ➞Law & practice ➞All Legal texts ➞London Agreement

In the case of a valid extension or validation

As regards translation requirements prescribed by the extension or validation states, please consult the website of the European Patent Office
www.epo.org ➞Law & practice ➞Legal texts, National law relating to the EPC

Failure to supply a prescribed translation in a contracting state, or in an extension or validation state may result in the patent being deemed to be void *ab initio* in the state concerned (Art. 65(3) EPC).

Petitioner's Exhibit 1022
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4.2 In the case of 2.2 above

If the present communication under Rule 71(3) EPC is based on an auxiliary request and, within the time limit, you maintain the main request or a higher ranking request which is not allowable, the application will be refused (Art. 97(2) EPC).

If the examining division gives its consent to the requested amendments or corrections, it will issue a new communication under Rule 71(3) EPC; otherwise, it shall resume the examination proceedings (Rule 71(6) EPC).

5. Filing of a divisional application

Any divisional application relating to this European patent application must be filed directly with the European Patent Office in Munich, The Hague or Berlin and will be in the language of the proceedings for the present application, or if the latter was not in an official language of the EPO, the divisional application may be filed in the language of the present application as filed (see Article 76(1) and Rule 36(2) EPC). Any such divisional application must be filed while the present application is still pending (Rule 36(1) EPC; Guidelines A-IV, 1.1.1).

6. Notes concerning fee payments

6.1 Making payments

For payments made via deposit account, please note that as from 1 December 2017 debit orders will only be carried out if filed in an electronically processable format (xml), using an accepted means of filing as laid down in the Arrangements for deposit accounts (ADA), published in the Supplementary publication in the Official Journal.

All relevant information related to the modes of payment of fees to the EPO can be retrieved from the EPO website at "**Making Payments**".

6.2 Information concerning fee amounts

Procedural fees are usually adjusted every two years, on even years, with effect from 1 April. Therefore, before making a payment, parties should verify the amounts actually due on the date of payment using the applicable version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, available on the EPO website (**www.epo.org**) at **www.epo.org/schedule-of-fees**. The "Schedule of fees" table allows the viewing, downloading and searching of individual fee amounts, both current and previous.

6.3 Note to users of the automatic debiting procedure

The fee for grant, including the fee for publication, and any additional claims fees due under Rule 71(4) EPC will be debited automatically on the date of filing of the translations of the claims, or on the last day of the period of this communication. However, if the designation fee(s) become(s) due as set out in Rule 71a(3) EPC and/or a renewal fee becomes due as set out in Rule 71a(4) EPC, these should be paid separately by another permitted way of payment in order not to delay the publication of the mention of the grant. The same applies in these circumstances to the payment of extension and validation fees. The same applies in these circumstances to the payment of extension and validation fees.

Note: If a waiver is expressed in response to a Rule 71(3) communication (see OJ EPO 2015, A52), the fee for grant, including the fee for publication/printing, and any additional claims fees will not be debited automatically. These fees must be paid separately by another means of payment allowed under the Rules relating to Fees.

Petitioner's Exhibit 1022
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Application No.: 14 185 786.2

IV.2. Patent classification

The classification indicated on the published patent application remains unchanged. It is as follows:

INV. A01N37/16 A01N25/00 A61K31/075 A61L9/00 A61L2/18 A61K31/327 A01P1/00

IV.3. Title of the invention

The title has been changed. It now is as follows:

Verfahren zur Erzeugung von Peressigsäure direkt am Verwendungsort

Method for the generation of peracetic acid on site at the point-of-use.

Procédé pour la génération d'acide peracétique sur site au niveau du point d'utilisation

IV.4. Documentation

28/02/18
Date

Bertrand, Franck
Chairman

Lorenzo Varela, M
1st examiner

Sawicki, Marcin
2nd examiner

Enclosure(s):

Petitioner's Exhibit 1022
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FIELD OF THE INVENITON

[0001] The invention relates to a method for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use.

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generated in-situ. It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519

A1.This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generated in-situ in the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a method of generating a non-equilibrium solution of peracetic acid, comprising:
a. providing water;
b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;
c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;
d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and
e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

[0020] The application discloses
a method of continuously or intermittently generating

a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be

contained in a mixing tank or other vessel.

The liquid acetyl precursor is triacetin. In accordance with the invention, the acetyl precursor and the aqueous hydrogen peroxide are introduced to the water separately, either sequentially, with either one first, or simultaneously.. The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within 30 seconds to five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. With triacetin used as the acetyl precursor and assuming all three acetyl groups are reacted, 40.9% to 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is 0.078% to 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of 11.2 to 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from 1% to 7.1%.

[0022] The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. The triacetin that is used as the acetyl precursor, is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[0026] The term "receiving water" means the water that is being treated.

[0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[0028] PAA and hydrogen peroxide in solution were determined using the ceric

sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate x 0.17}}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate x 0.38}}{\text{wt . sample}}$$

[0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[0030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD),

which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[0031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

3. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

[0035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[0036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate

should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[0037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is 5.6% to 22.5% of the total.

[0041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at

which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[0042] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0043] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For example, with 1.9×10^{-2} m (3/4 ") pipe, a static mixer of 1.9×10^{-2} m (3/4 ") diameter and 6" long, and a velocity of 6.3×10^{-5} m^3/s (1 gal/min), mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0044] An aqueous source of an alkali metal or earth alkali metal hydroxide is

provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0045] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is 1.82% to 7.28% of the total amount. With the acetyl precursor as triacetin, a mole ratio of NaOH: hydrogen peroxide:triacetin is 4.2:3.8:1.

[0046] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0047] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[0048] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor

employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within 30 seconds to five minutes.

[0050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[0052] The application further discloses

a method of continuously or intermittently generating

a non-equilibrium solution of PAA on a site having the point-of-use in a batch process comprises the following steps:

(a) Providing water.

A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0054] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is 5.6% to 22.5% of the total.

[0056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either

simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is 1.82% to 7.28% of the total amount. With the acetyl precursor as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is 4.2:3.8:1.

[0061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within 30 seconds to five minutes.

[0064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$H_2O_2=H^+ + HO_2-$

[0066] The perhydroxyl anion (HO_2-) then affects nucleophilic substitution reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. With the acetyl precursor as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. With triacetin used, assuming all three acetyl groups are reacted,

40.9% to 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is 0.078% to 1.88%.

[0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from 1% to 7.1%. In addition, the PAA solutions are alkaline, having a pH of 11.2 to 13.37.

[0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example 1

[0072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

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Table VIII

t #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

Example 2

[0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

Example 3

[0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6

5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes.

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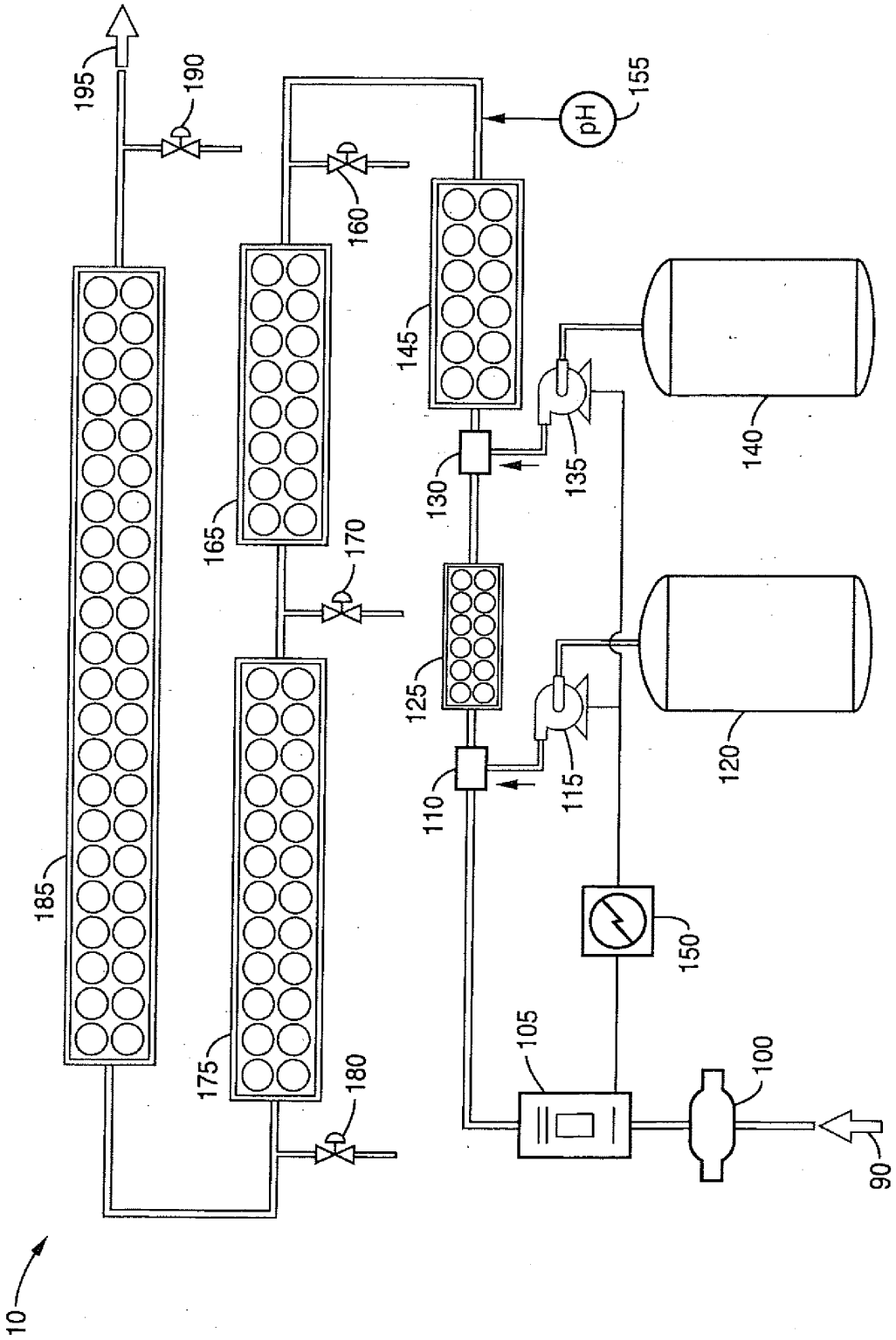

195
190
155
pH
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145
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130
165
170
125
120
115
110
185
150
105
100
175
180
90
10

FIG. 1

FIELD OF THE INVENITON

[0001] The invention relates to 2 a method 2 ~~liquid compositions and methods of using the liquid compositions~~ for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. ~~The invention also relates to a solid bleaching and stain removal composition.~~

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water ~~(about~~ 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generated in-situ. It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519

A1.This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generated in-situ in the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a 2 ▛ method of generating a non-equilibrium solution of peracetic acid, comprising: ¶

a. providing water; ¶

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first; ¶

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture; ¶

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and ¶

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1. ▟

2 ~~method of generating a non-equilibrium solution of peracetic acid as defined by claim 1~~.

[0020] The application discloses ~~A further embodiment is~~ a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be

contained in a mixing tank or other ~~vessel.~~ vessel. The liquid acetyl precursor is triacetin. In accordance with the invention, the acetyl precursor and the aqueous hydrogen peroxide are introduced to the water separately, either sequentially, with either one first, or simultaneously.. The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within ~~about~~ 30 seconds to ~~about~~ five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. With triacetin used as the acetyl precursor and assuming all three acetyl groups are reacted, ~~about~~ 40.9% to ~~about~~ 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is ~~about~~ 0.078% to ~~about~~ 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of ~~about~~ 11.2 to ~~about~~ 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from ~~about~~ 1% to ~~about~~ 7.1%.

[0022] The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. The triacetin that is used as the acetyl precursor, is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[0026] The term "receiving water" means the water that is being treated.

[0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[0028] PAA and hydrogen peroxide in solution were determined using the ceric

sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate x 0.17}}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate x 0.38}}{\text{wt . sample}}$$

[0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[0030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD),

which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[0031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

3. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

[0035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[0036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate

should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[0037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is ~~about~~ 5.6% to ~~about~~ 22.5% of the total.

[0041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at

which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[0042] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0043] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For example, with 2 1.9 X 10^{-2} m (3/4 ") 2 ~~3/4"~~ pipe, a static mixer of 2 1.9 X 10-2 m (3/4 ") 2 ~~3/4"~~ diameter and 6" long, and a velocity of ~~about~~ 2 6.3 x 10^{-5} m^3/s (1 gal/min) 2 ~~1 gal/min~~. , mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0044] An aqueous source of an alkali metal or earth alkali metal hydroxide is

provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0045] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is ~~about~~ 1.82% to ~~about~~ 7.28% of the total amount. With the acetyl precursor as triacetin, a mole ratio of NaOH: hydrogen peroxide:triacetin is ~~about~~ 4.2:3.8:1.

[0046] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0047] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[0048] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor

employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within ~~about~~ 30 seconds to ~~about~~ five minutes.

[0050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[0052] The application further discloses ~~In another embodiment,~~ a method of continuously or intermittently generating

a non-equilibrium solution of PAA on a site having ~~a~~ the point-of-use in a batch process comprises the following steps:

(a) Providing water.

A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0054] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is ~~about~~ 5.6% to ~~about~~ 22.5% of the total.

[0056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either

simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is ~~about~~ 1.82% to ~~about~~ 7.28% of the total amount. With the acetyl precursor as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is ~~about~~ 4.2:3.8:1.

[0061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within ~~about~~ 30 seconds to ~~about~~ five minutes.

[0064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$H_2O_2=H^+ + HO_2-$

[0066] The perhydroxyl anion (HO_2-) then affects nucleophilic substitution reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. With the acetyl precursor as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. With triacetin used, assuming all three acetyl groups are reacted,

~~about~~ 40.9% to ~~about~~ 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is ~~about~~ 0.078% to ~~about~~ 1.88%.

[0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from ~~about~~ 1% to ~~about~~ 7.1%. In addition, the PAA solutions are alkaline, having a pH of ~~about~~ 11.2 to ~~about~~ 13.37.

[0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example 1

[0072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

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Table VIII

t #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

Example 2

[0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to ~~about~~ 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of ~~about~~ 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

Example 3

[0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6

5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes.

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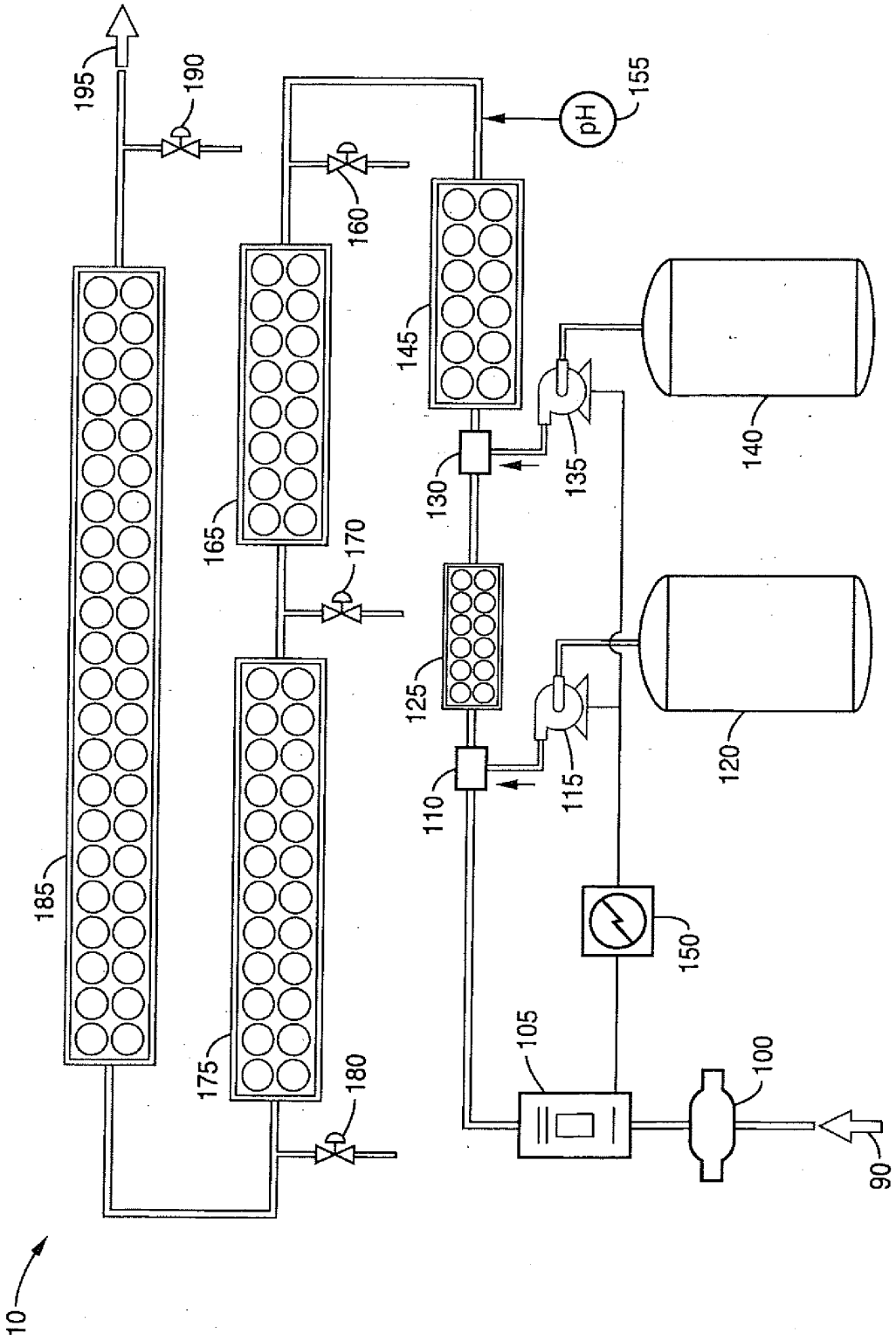

195
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FIG. 1

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Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	6047125	
Application number	EP14185786.2	
Date of receipt	13 February 2018	
Receiving Office	European Patent Office, The Hague	
Your reference	X11031DIV2-EP	
Applicant	All applicants as on file	
Documents submitted	package-data.xml epf1038.pdf (1 p.)	ep-sfd-request.xml
Submitted by	CN=David Corbyn 29824	
Method of submission	Online	
Date and time receipt generated	13 February 2018, 10:55 (CET)	
Message Digest	37:AE:34:E5:CE:4C:76:E7:6F:68:9C:8C:EB:F9:87:DC:C9:E0:6B:20	

Correction by the EPO of errors in debit instructions filed by eOLF
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Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number	14185786.2
Applicant's or representative's reference	X11031DIV2-EP

	Description of document	Original file name	Assigned file name

	Fees	Factor applied	Fee schedule	Amount to be paid
15-1	038 Renewal fee for the 8th year	1	1 280.00	1 280.00
	Total:		**EUR**	**1 280.00**

	Payment	
1	Method of payment	Debit from deposit account
	Currency:	EUR
	The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.	
	Deposit account number:	28050202
	Account holder:	Bailey Walsh & Co
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Signatures

Place:	**Leeds**
Date:	**12 February 2018**
Signed by:	**David Corbyn 29824**
Representative name:	**Alexandra Tomkinson**
Capacity:	**(Representative)**

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes ~~to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid~~.

~~3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.~~

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

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c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes.

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Our ref.: X11031DIV2-EP
18 January 2018

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In relation to the above-mentioned application, this is the Applicant's response to the Communication from the Examining Division pursuant to Article 94(3) EPC, dated 27 July 2017. The Applicant files herewith, a set of amended claims to replace those currently on file. A copy of the claims showing the amendments now made is also included for the Examiner's convenience.

Claim Amendments

Claim 1 has been amended to include the features of previous claim 3, wherein the mole ratio of sodium hydroxide to hydrogen peroxide to triacetin in 4.2:3.8:1. Claim 3 has subsequently been deleted.

Claim 2 has been amended to specify the reaction medium is allowed "a reaction time of 30 seconds to 5 minutes." The phrase defined the result being achieved by this reaction time has been removed.

Objections in the Report

Referring now to the comments in the examination report, the Examiner has now raised a new objection to claims 1-3, alleging that they lack an inventive step over prior art documents D1 and D5 - this despite there being no such objections in the previous

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examination report. Furthermore, the subject matter of the combination of at least original claims 1, 6 and 7 (previous claim 1) was deemed to be both novel and inventive over the prior art in the European search opinion.

While the Applicant disagrees with the Examiner's current objections, claim 1 has been further amended as discussed above to include the features of previous claim 3, and the Applicant submits that amended claim 1 is both novel and inventive over the cited prior art.

The process in D5 (see page 4, lines 19-24) uses far more sodium hydroxide than that required in the present invention. D5 discloses 1 part sodium hydroxide to 4 parts TAED by weight. The molecular weight of sodium hydroxide is 40; the molecular weight of TAED is 228. Thus, a ratio by weight of 1 part sodium hydroxide to 4 parts TAED is equal to a mole ratio of sodium hydroxide to TAED of 25:1. D5 also discloses ratios of 1 part sodium hydroxide to 3 parts TAED by weight, and 1 part sodium hydroxide to 2 parts TAED by weight. The latter ratio of 1 part to 2 parts by weight is equal to a mole ratio of sodium hydroxide to TAED of 12.5:1. Thus, D5 discloses mole ratios of sodium hydroxide to TAED of 12.5:1 to 25:1. Amended claim 1 of the present invention requires a mole ratio of sodium hydroxide to hydrogen peroxide to triacetin of 4.2:3.8:1, that is to say, the mole ratio of sodium hydroxide to triacetin is 4.2:1, which is far less than the range of mole ratios using TAED of 12.5:1 to 25:1 disclosed in D5.

Furthermore, providing a method of preparing a solution of peracetic acid not at equilibrium, using sodium hydroxide in the claimed range of wt% in claim 1, is simply not disclosed or even alluded to in the prior art. The Examiner alleges that starting from D5 the skilled person would simply substitute TAED for triacetin and arrive at the present invention, but gives no consideration to the amounts of each compound required, in particular, the optimum amount of sodium hydroxide. As demonstrated in the description, the claimed wt% of sodium hydroxide required (1.82% - 7.28% by weight) show the rapid generation of PAA, which provides the non-equilibrium solutions with some unique characteristics: the PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

Finally, the Examiner has indicated that if the above objections are not overcome, a summons to oral proceedings can be expected as a next step. The Applicant respectfully submits, however, that this is the first instance in which the above objections to novelty and inventiveness have been raised, and the Examiner has contradicted the original view provided in the search opinion with regard to the wt% of sodium hydroxide. We therefore submit that if the above comments are not sufficient to overcome the Examiner's objections, at least one further examination report should be issued.

With the above in mind, it is respectfully submitted that the amended claims are both

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novel and inventive over the cited prior art documents, in accordance with Articles 54 and 56 EPC.

Referring now to the Examiner's comments regarding the description, it is respectfully submitted that the amended pages of the description filed with the Applicant's response dated 7 September 2015 brings it into conformity with the claims. Significant portions of the description have been deleted and what remains relate entirely to the method as claimed in the present claims, and examples thereof. Furthermore, paragraph [0019] in the amended description clearly refers to claim 1, and the subsequent description goes into specific detail of each step. It is therefore respectfully submitted that the claims and description are clear, in accordance with Article 84 EPC.

We trust the amendments and arguments are sufficient to overcome the Examiner's objections and we look forward to receiving confirmation to this effect in due course. In the event the Examiner intends to reject the application without providing any further opportunity for written comment, we hereby request oral proceedings under Article 116 EPC.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes ~~to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid~~.

~~3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.~~

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Duration: 01.18.2018 09:34:02 AM - 01.18.2018 09:38:18 AM. This page 4 of 5 was completed at 01.18.2018 09:37:48 AM

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight, and wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

2. The method of claim 1, further comprising allowing the reaction medium a reaction time of 30 seconds to five minutes.

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Duration: 01.18.2018 09:34:02 AM - 01.18.2018 09:38:18 AM. This page 5 of 5 was completed at 01.18.2018 09:38:18 AM

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Associates: M. Kellett, MITMA
D. Corbyn, MChem (Hons), CPA, EPA

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BY FACSIMILE
CONFIRMATION TO FOLLOW BY POST
00 4989 2399 4465

Our ref.: X11031DIV2-EP
18 January 2018

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In relation to the above-mentioned application, this is the Applicant's response to the Communication from the Examining Division pursuant to Article 94(3) EPC, dated 27 July 2017. The Applicant files herewith, a set of amended claims to replace those currently on file. A copy of the claims showing the amendments now made is also included for the Examiner's convenience.

Claim Amendments

Claim 1 has been amended to include the features of previous claim 3, wherein the mole ratio of sodium hydroxide to hydrogen peroxide to triacetin in 4.2:3.8:1. Claim 3 has subsequently been deleted.

Claim 2 has been amended to specify the reaction medium is allowed "a reaction time of 30 seconds to 5 minutes." The phrase defined the result being achieved by this reaction time has been removed.

Objections in the Report

Referring now to the comments in the examination report, the Examiner has now raised a new objection to claims 1-3, alleging that they lack an inventive step over prior art documents D1 and D5 - this despite there being no such objections in the previous

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Received at the EPO on Jan 18, 2018 09:38:18. Page 1 of 5
Duration: 01.18.2018 09:34:02 AM - 01.18.2018 09:38:18 AM. This page 1 of 5 was completed at 01.18.2018 09:35:15 AM

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IPR2025-01471 – Page 085

examination report. Furthermore, the subject matter of the combination of at least original claims 1, 6 and 7 (previous claim 1) was deemed to be both novel and inventive over the prior art in the European search opinion.

While the Applicant disagrees with the Examiner's current objections, claim 1 has been further amended as discussed above to include the features of previous claim 3, and the Applicant submits that amended claim 1 is both novel and inventive over the cited prior art.

The process in D5 (see page 4, lines 19-24) uses far more sodium hydroxide than that required in the present invention. D5 discloses 1 part sodium hydroxide to 4 parts TAED by weight. The molecular weight of sodium hydroxide is 40; the molecular weight of TAED is 228. Thus, a ratio by weight of 1 part sodium hydroxide to 4 parts TAED is equal to a mole ratio of sodium hydroxide to TAED of 25:1. D5 also discloses ratios of 1 part sodium hydroxide to 3 parts TAED by weight, and 1 part sodium hydroxide to 2 parts TAED by weight. The latter ratio of 1 part to 2 parts by weight is equal to a mole ratio of sodium hydroxide to TAED of 12.5:1. Thus, D5 discloses mole ratios of sodium hydroxide to TAED of 12.5:1 to 25:1. Amended claim 1 of the present invention requires a mole ratio of sodium hydroxide to hydrogen peroxide to triacetin of 4.2:3.8:1, that is to say, the mole ratio of sodium hydroxide to triacetin is 4.2:1, which is far less than the range of mole ratios using TAED of 12.5:1 to 25:1 disclosed in D5.

Furthermore, providing a method of preparing a solution of peracetic acid not at equilibrium, using sodium hydroxide in the claimed range of wt% in claim 1, is simply not disclosed or even alluded to in the prior art. The Examiner alleges that starting from D5 the skilled person would simply substitute TAED for triacetin and arrive at the present invention, but gives no consideration to the amounts of each compound required, in particular, the optimum amount of sodium hydroxide. As demonstrated in the description, the claimed wt% of sodium hydroxide required (1.82% - 7.28% by weight) show the rapid generation of PAA, which provides the non-equilibrium solutions with some unique characteristics: the PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

Finally, the Examiner has indicated that if the above objections are not overcome, a summons to oral proceedings can be expected as a next step. The Applicant respectfully submits, however, that this is the first instance in which the above objections to novelty and inventiveness have been raised, and the Examiner has contradicted the original view provided in the search opinion with regard to the wt% of sodium hydroxide. We therefore submit that if the above comments are not sufficient to overcome the Examiner's objections, at least one further examination report should be issued.

With the above in mind, it is respectfully submitted that the amended claims are both

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Received at the EPO on Jan 18, 2018 09:38:18. Page 2 of 5
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novel and inventive over the cited prior art documents, in accordance with Articles 54 and 56 EPC.

Referring now to the Examiner's comments regarding the description, it is respectfully submitted that the amended pages of the description filed with the Applicant's response dated 7 September 2015 brings it into conformity with the claims. Significant portions of the description have been deleted and what remains relate entirely to the method as claimed in the present claims, and examples thereof. Furthermore, paragraph [0019] in the amended description clearly refers to claim 1, and the subsequent description goes into specific detail of each step. It is therefore respectfully submitted that the claims and description are clear, in accordance with Article 84 EPC.

We trust the amendments and arguments are sufficient to overcome the Examiner's objections and we look forward to receiving confirmation to this effect in due course. In the event the Examiner intends to reject the application without providing any further opportunity for written comment, we hereby request oral proceedings under Article 116 EPC.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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Questions about this communication ?
Contact Customer Services at www.epo.org/contact

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Date
04.12.17

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Extension of time limit pursuant to Rule 132(2) EPC

Examination procedure

With reference to your request, the time limit for replying to the communication pursuant to Article 94(3) EPC dated 27.07.17 has been extended

by 2 months

to a total of 6 months

from the date of notification of the above-mentioned communication.

Please note: To the extent that your request exceeded the above extension, your request has been refused.

Note
The granting of extensions to time limits is governed by the Implementing Regulations to the EPC and the Guidelines for Examination in the EPO, E-VIII, 1.6. A request for extension, which would result in the total period set exceeding six months, must be reasoned and supported by evidence.

If no reply to the communication is received in due time, the European patent application will be deemed to be withdrawn (Art. 94(4) EPC).

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Important information in case of a PACE request
If a PACE request has been validly filed for the application, the applicant is herewith informed that with the grant of the request for extension of time limit the application is removed from the PACE programme. A second PACE request for that application during the same stage of the procedure will not be processed (see OJ EPO 2015, A93, point 4).

For the Examining Division



Petitioner's Exhibit 1022
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IPR2025-01471 – Page 089

EPO - Munich
102
04. Dez. 2017

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Associates: M. Kellett, MITMA
D. Corbyn, MChem (Hons), CPA, EPA

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D-80298 Munich
Germany

Confirmation only
already sent by fax

BY FACSIMILE
CONFIRMATION TO FOLLOW BY POST
00 4989 2399 4465

Our ref.: DC-X11031DIV2-EP
29 November 2017

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In relation to the above matter and further to the examination report, dated 27 July 2017, we hereby request a two month extension of time for providing a response, available as of right.

We look forward to receiving confirmation to this effect in due course.

Yours faithfully,
BAILEY WALSH & CO LLP

D. Corbyn

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29 November 2017

Dear Sirs,

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Yours faithfully,
BAILEY WALSH & CO LLP

D. Corbyn

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Received at the EPO on Nov 29, 2017 12:57:28. Page 1 of 1
Duration: 11.29.2017 12:56:58 PM - 11.29.2017 12:57:28 PM. This page 1 of 1 was completed at 11.29.2017 12:57:28 PM

The examination is being carried out on the **following application documents**

Description, Pages

1-24	received on	07-09-2015	with letter of	07-09-2015

Claims, Numbers

1-3	received on	17-07-2017	with letter of	17-07-2017

Drawings, Sheets

1/1	as originally filed

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 EP 1 618 786 A1 (KAO CORP [JP]) 25 January 2006 (2006-01-25)

D2 JP 2004 230323 A (MATSUSHITA ELECTRIC IND CO LTD) 19 August 2004 (2004-08-19)

D3 US 2010/227000 A1 (AMES KELLY ANN [GB] ET AL BOARD KELLY ANN [GB] ET AL) 9 September 2010 (2010-09-09)

D4 US 6 221 341 B1 (MONTGOMERY R ERIC [US]) 24 April 2001 (2001-04-24)

D5 WO 01/46519 A1 (WARWICK INTERNAT GROUP LTD [GB]; WITHENSHAW JOHN DAVID [GB]; SKETT MAT) 28 June 2001 (2001-06-28)

1. The present application concerns a method for generating a non-equilibrium solution of peracetic acid in water. A solution of hydrogen peroxide and triacetin are added to water separately and an aqueous solution of sodium hydroxide (the sodium hydroxide at 1.82% to 7.28% weight) is added to the mixture and stirred. The method

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is used in mixing tanks and under aqueous stream. Non-equilibrium solutions of peroxycarboxylic acid are cost effective and safer because they do not require high concentration of hazardous reagent to be stored or transported.

Inventive step

2. The subject-matter of claims 1-3 does not involve an inventive step in the sense of Art. 56 EPC.

D5 is considered to be the closest prior-art since it also concerns a continuous way of producing a non-equilibrium sanitizing solution of peracetic acid (p. 3, lines 6 to 10). The difference with the claimed method is in the acetyl source used.

D1 discloses the use of triacetin as the acetyl source in the preparation of compositions comprising peracetic acid in water.

The problem to be solved in the application can not be seen in the provision of an improved method taking into account that no comparative example has been carried out with respect to the closest state of the art and therefore, there is no evidence in the application of an improvement or unexpected effects over the closest prior art, D5. Therefore, the technical problem to be solved must be formulated in a less ambitious way as the provision of merely an alternative method of preparing a non-equilibrium solution of peracetic acid.

The solution proposed in the application consists in the method according to claim 1.

Selecting a specific alternative acetyl source from those ones well known in the art from D1 or from D3, namely triacetin, for providing merely an alternative method of producing a non-equilibrium sanitizing solution of peracetic acid without having any unexpected effect is obvious for the person skilled in the art. It is within the ambit of the person skilled in the art seeking to solve the less ambitious technical problem underlying the present patent application of providing merely a further method of producing a non-equilibrium sanitizing solution of peracetic acid to consider routinely any conceivable modification of the closest prior art process and its combination with the teaching of another document of the state of the art, such as D1 or D3. The applicant argues in the description that the present claimed process avoids the use of a solid such as TAED used in the closest state of the art. However, even if this would have been a problem in the process the person skilled in the art would have looked for liquid alternatives to the acetyl source and would have found them in D1 or D3, leading to the present claimed process without the need of inventive skills. Introducing the hydrogen peroxide and triacetin together or separately to water are obvious alternatives without any unexpected effects in view of the description of the present

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application. The present claimed process is therefore regarded as obvious for the skilled person in the art and therefore, lacking inventive step. Hence, no inventive step can be acknowledged.

Further comments

3. The description refers as well to liquid compositions as falling under the scope of protection. However, the claims confer only protection for the method of preparation and the composition is only protected as far as it is produced by the present method, not in general. Hence, the description is not properly adapted to the claims, contrary to Art. 84 EPC.

4. The description is not properly adapted to the claims, contrary to Art. 84 EPC. There is no counterpart in the description to present claim 1.

5. It is clear from the description on pages 15 and 16 and the examples that the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin being 4.2:3.8:1 is essential to the definition of the invention.

Since independent claim 1 does not contain this feature it does not meet the requirement following from Article 84 EPC, taken in combination with Rule 43(1) and (3) EPC, that any independent claim must contain all the technical features essential to the definition of the invention.

6. Claim 2 does not meet the requirements of Article 84 EPC in that the matter for which protection is sought is not defined. The claim attempts to define the subject-matter in terms of the result to be achieved. Such a definition is only allowable under the conditions elaborated in the Guidelines F-IV, 4.10. In this instance, however, such a formulation is not allowable because it appears possible to define the subject-matter in more concrete terms, viz. in terms of how the effect is to be achieved.

7. If the applicant does not overcome all the above-mentioned objections with his next answer, he should expect as the next official action an invitation to attend oral proceedings upon request with a foreseen refusal.

8. When filing amended claims the applicant should at the same time bring the description into conformity with the amended claims.

9. In order to facilitate the examination of the conformity of the amended application with the requirements of Article 123(2) EPC, the applicant should clearly identify the amendments carried out, irrespective of whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based.

The applicant should submit these indications additionally in handwritten form on a copy of the relevant parts of the application as filed.

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Application No.	Ref.	Date
14 185 786.2 - 1454	AT-BF-G49415	27.07.2017
Applicant Enviro Tech Chemical Services Inc.		

Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

of 4 months

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).

Registered letter

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 095

Lorenzo Varela, M
Primary Examiner
For the Examining Division

Enclosure(s): 3 page/s reasons (Form 2906)

Registered letter
EPO Form 2001 11.16TRI

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

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Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 098

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P. Stephenson, MSci, PhD, MRSC, CPA, EPA
Associates: M. Kellett, MITMA
D. Corbyn, MChem (Hons), CPA, EPA

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101
17. Juli 2017

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D-80298 Munich
Germany

Confirmation only already sent by fax

BY FACSIMILE
CONFIRMATION TO FOLLOW BY POST
00 4989 2399 4465

Our ref.: DC-X11031DIV2-EP
10 July 2017

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In relation to the above-mentioned application, this is the Applicant's response to the Communication from the Examining Division pursuant to Article 94(3) EPC, dated 6 March 2017. The Applicant files herewith, a set of amended claims to replace those currently on file. A copy of the claims showing the amendments now made is also included for the Examiner's convenience.

Claim Amendments

Claim 1 has been amended to include, in step (b), that the triacetin and the aqueous hydrogen peroxide are introduced to the water separately, either simultaneously or sequentially, with either one first. Basis for this inclusion may be found in paragraph [0113] of the application as originally filed.

Objections in the Report

Referring now to the objections raised in the examination report, the Examiner has, firstly, objected to claim 2 as introducing subject matter extending beyond the scope of the application as originally filed. The Applicant respectfully disagrees with this assertion.

The Examiner is alleging that there is no support in the application for the combination of

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original claims 1, 6, 7, 9 and 10 (now the combination of claims 1 and 2). However, support for this combination is present in the description. Current claim 1 is a method of steps (a) through (e). There are two different embodiments of this method described in the specification: paras. 81-104; and para. 105-126.
Step (a) is described in paras. 83-86; and 106-107.
Step (b) is described in paras. 87-92, in particular para. 92; and 108-113, in particular para. 113.
Step (c) is described in paras. 93-94; and 114-115.
Step (d) is described in paras. 95-100; and 116-120.
Step (e) is described in paras. 97, 101-104; and 118, 121-126.

Present claim 2 (based on original claims 1, 9 and 10) states that the method further comprises a step of allowing the reaction medium formed in step (e) 30 seconds to 5 minutes to maximize the conversion of the hydrogen peroxide and triacetin to peracetic acid. This time period is described with respect to both embodiments at para. 104 and para. 126. It is clear from the description, therefore, that this time period is applicable to the method described in steps (a) through (e).

Finally, claim 3 (based on original claims 1, 6 and 12) describes the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin as being 4.2:3.8:1. This mole ratio is described with respect to both embodiments at para. 97 and para. 118. It is clear from the specification that this mole ratio is applicable to the method described in steps (a) through (e).

With the above in mind, it is respectfully submitted that the present claims not only satisfy the requirements of Article 123(2) EPC, but also those of Article 76(1) EPC.

With respect to the issue of double patenting, an objection which the Examiner has maintained, the Applicant reasserts their previous arguments, but submits that amended claim 1 serves to distinguish the present claims from those of the parent further – claim 1 of the parent application requires the introduction of a single component ("a hydrogen peroxide-triacetin solution") to the water; amended claim 1 of the present application requires the introduction of two separate components, and this distinction is made all the clearer now that it is specified clearly in the claim that the two components are added "*separately, either simultaneously or sequentially, separately, with either one first*". Adding such components separately, rather than as a single solution, is a significant difference, as explained in the Applicant's previous response, dated 25th November 2016. Support for introducing two separate components is also present in the description, and may be found in paras. 92 and 113.

Regarding the novelty and inventiveness of the claims, it is noted that the claims were deemed to be both novel and inventive over the cited prior art documents in the extended European search report, dated 30th January 2015, and it is submitted that this novelty and

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inventiveness is maintained in the presently amended claims.

We trust the amendments and arguments are sufficient to overcome the Examiner's objections and we look forward to receiving confirmation to this effect in due course. In the event the Examiner intends to reject the application without providing any further opportunity for written comment, we hereby request oral proceedings under Article 116 EPC.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

Duration: 10.07.2017 12:52:59 - 10.07.2017 12:53:38. This page 4 of 5 was completed at 10.07.2017 12:53:32
Received at the EPO on Jul 10, 2017 12:53:38. Page 4 of 5

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 102

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water separately, either simultaneously or sequentially, with either one first;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

Duration: 10.07.2017 12:52:59 - 10.07.2017 12:53:38. This page 5 of 5 was completed at 10.07.2017 12:53:38
Received at the EPO on Jul 10, 2017 12:53:38. Page 5 of 5

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Associates: M. Kellett, MITMA
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Our ref.: DC-X11031DIV2-EP
10 July 2017

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In relation to the above-mentioned application, this is the Applicant's response to the Communication from the Examining Division pursuant to Article 94(3) EPC, dated 6 March 2017. The Applicant files herewith, a set of amended claims to replace those currently on file. A copy of the claims showing the amendments now made is also included for the Examiner's convenience.

Claim Amendments

Claim 1 has been amended to include, in step (b), that the triacetin and the aqueous hydrogen peroxide are introduced to the water separately, either simultaneously or sequentially, with either one first. Basis for this inclusion may be found in paragraph [0113] of the application as originally filed.

Objections in the Report

Referring now to the objections raised in the examination report, the Examiner has, firstly, objected to claim 2 as introducing subject matter extending beyond the scope of the application as originally filed. The Applicant respectfully disagrees with this assertion.

The Examiner is alleging that there is no support in the application for the combination of

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original claims 1, 6, 7, 9 and 10 (now the combination of claims 1 and 2). However, support for this combination is present in the description. Current claim 1 is a method of steps (a) through (e). There are two different embodiments of this method described in the specification: paras. 81-104; and para. 105-126.
Step (a) is described in paras. 83-86; and 106-107.
Step (b) is described in paras. 87-92, in particular para. 92; and 108-113, in particular para. 113.
Step (c) is described in paras. 93-94; and 114-115.
Step (d) is described in paras. 95-100; and 116-120.
Step (e) is described in paras. 97, 101-104; and 118, 121-126.

Present claim 2 (based on original claims 1, 9 and 10) states that the method further comprises a step of allowing the reaction medium formed in step (e) 30 seconds to 5 minutes to maximize the conversion of the hydrogen peroxide and triacetin to peracetic acid. This time period is described with respect to both embodiments at para. 104 and para. 126. It is clear from the description, therefore, that this time period is applicable to the method described in steps (a) through (e).

Finally, claim 3 (based on original claims 1, 6 and 12) describes the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin as being 4.2:3.8:1. This mole ratio is described with respect to both embodiments at para. 97 and para. 118. It is clear from the specification that this mole ratio is applicable to the method described in steps (a) through (e).

With the above in mind, it is respectfully submitted that the present claims not only satisfy the requirements of Article 123(2) EPC, but also those of Article 76(1) EPC.

With respect to the issue of double patenting, an objection which the Examiner has maintained, the Applicant reasserts their previous arguments, but submits that amended claim 1 serves to distinguish the present claims from those of the parent further – claim 1 of the parent application requires the introduction of a single component ("a hydrogen peroxide-triacetin solution") to the water; amended claim 1 of the present application requires the introduction of two separate components, and this distinction is made all the clearer now that it is specified clearly in the claim that the two components are added "*separately, either simultaneously or sequentially, separately, with either one first*". Adding such components separately, rather than as a single solution, is a significant difference, as explained in the Applicant's previous response, dated 25th November 2016. Support for introducing two separate components is also present in the description, and may be found in paras. 92 and 113.

Regarding the novelty and inventiveness of the claims, it is noted that the claims were deemed to be both novel and inventive over the cited prior art documents in the extended European search report, dated 30th January 2015, and it is submitted that this novelty and

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inventiveness is maintained in the presently amended claims.

We trust the amendments and arguments are sufficient to overcome the Examiner's objections and we look forward to receiving confirmation to this effect in due course. In the event the Examiner intends to reject the application without providing any further opportunity for written comment, we hereby request oral proceedings under Article 116 EPC.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 106

The examination is being carried out on the **following application documents**

Description, Pages

1-59 as originally filed

Claims, Numbers

1-3 filed with telefax on 07-09-2015

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 EP 1 618 786 A1 (KAO CORP [JP]) 25 January 2006 (2006-01-25)

D2 JP 2004 230323 A (MATSUSHITA ELECTRIC IND CO LTD) 19 August 2004 (2004-08-19)

D3 US 2010/227000 A1 (AMES KELLY ANN [GB] ET AL BOARD KELLY ANN [GB] ET AL) 9 September 2010 (2010-09-09)

D4 US 6 221 341 B1 (MONTGOMERY R ERIC [US]) 24 April 2001 (2001-04-24)

D5 WO 01/46519 A1 (WARWICK INTERNAT GROUP LTD [GB]; WITHENSHAW JOHN DAVID [GB]; SKETT MAT) 28 June 2001 (2001-06-28)

1. The present application relates to a method for generating a non-equilibrium solution of peracetic acid in water. Triacetin and aqueous hydrogen peroxide and triacetin are added water and a solution of a metal hydroxide is added to the mixture and stirred, forming a reaction medium comprising a non-equilibrium solution of peracetic acid, **characterized in that** the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

Art. 123(2) EPC

2. The amendments filed on 07-09-2015 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 123(2) EPC. The amendments concerned are the following: **claim 2**, taking into account that it includes

the subject-matter of claims 9 and 10 as originally filed, which were dependent on claim 1 as originally filed. As present claim 1 now comprises the subject-matter of claims 6 and 7 as originally filed and present claim 2 depends on present claim 1, there is no basis for the subject-matter of present claim 2 in the application as originally filed, taking into account that no disclosure of the subject-matter of present claim 2 in combination with the one of present claim 1 is present in the description as originally filed.

Art. 76(1) EPC

3. No basis can be found in the parent application as originally filed for the subject-matter of the present claims. Therefore, the requirements of Art. 76(1) EPC are not fulfilled. The applicant is kindly requested to indicate where in the parent application as originally filed can be found basis for the subject-matter of the present claims.

Double patenting

4. The applicant indicates that the subject-matter of this divisional application differs from the one of the parent application in the fact that in the parent an aqueous solution comprising triacetin and hydrogen is mixed with water whilst in the present application triacetin and aqueous hydrogen peroxide are used as two different entities. However, this is a narrow interpretation of present claim 1, which comprises as well that triacetin and aqueous hydrogen peroxide are together in a single solution. Therefore, there is an overlap between the subject-matter granted in the parent application and the one in the divisional application; moreover, it appears that no basis for the interpretation given by the applicant to the present claims can be found in the parent application as originally filed at least for all the technical features of the present claims. A clarification is needed.

The practice of the EPO first instance departments is not to allow that the parent and divisional applications claim identical subject-matter (see Guidelines for Examination, C-IV, 7.4 and C-VI, 9.1.6). This practice was confirmed in G1/05 and G1/06 (OJ EPO 2008, 271 and 307 respectively, Reasons 13.4).

It is a generally recognised principle of procedural law that a person can be granted only one European patent for the same invention in respect of which there are several applications with the same date of filing or, where priority is claimed, with the same date of priority. Moreover, the prevention of double patenting is a specific expression of the general principle of legitimate interest in the proceedings, which itself is a generally recognised principle of procedural law applicable under Article 125 EPC.

Novelty and inventive step

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 108

5. In case the applicant can overcome the above-mentioned objections, he is requested to indicate the difference of the claimed subject-matter with respect to any of the above-mentioned documents of the prior art (D1-D5), to choose one as closest prior art, to formulate the problem-solution approach and to indicate why the present claimed subject-matter is inventive over the closest state of the art and it is not suggested by any of the available documents of the prior art.

Further comments

6. If the applicant cannot overcome all above-mentioned objections in his next communication, he should expect as the next official action an invitation to attend oral proceedings upon request.

7. When filing amended claims the applicant should at the same time bring the description into conformity with the amended claims in order to speed up the procedure.

8. In order to facilitate the examination of the conformity of the amended application with the requirements of Article 123(2) EPC, the applicant should clearly identify the amendments carried out, irrespective of whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based (see Guidelines E-II, 1).

9. The applicant should submit these indications additionally in handwritten form on a copy of the relevant parts of the application as filed.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 109

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Substantive Examiner
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Tel: +49 89 2399 - 8239

Application No.	Ref.	Date
14 185 786.2 - 1454	AT-BF-G49415	06.03.2017
Applicant Enviro Tech Chemical Services Inc.		

Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

of 4 months

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).

Registered letter

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 110

Lorenzo Varela, M
Primary Examiner
For the Examining Division

Enclosure(s): 3 page/s reasons (Form 2906)

Registered letter
EPO Form 2001 11.16TRI

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Associates: P. Stephenson, MSci, PhD, MRSC, CPA, EPA
M. Kellett, MITMA
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23. Jan. 2017

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Our ref: X11031DIV2-EP
16 January 2017

Dear Sirs

Re: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Would you please deduct **€1165.00** from our Account No. 28050202 in payment of the 7th annuity due on the above application before the end of March 2017.

Yours faithfully
BAILEY WALSH & CO. LLP
Bailey Walsh + Co

zur Kasse

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EP 14185786.2

PCT

Code		Amount/EUR	Code		Amount/EUR
001	Filing fee – EP direct[3]		010	Opposition fee	
501	Additional fee (more than 35 pages)		011	Fee for appeal	
020	Filing fee – entry EP phase[3] (Rule 159(1)(c) EPC)		029	Certified copy of application; priority document	
520	Additional fee (more than 35 pages) – entry EP phase		033	Renewal fee for the 3rd year	
	Additional fee for divisional applications (Rule 38(4)EPC)[9]		034	Renewal fee for the 4th year	
002	Fee for a European search		035	Renewal fee for the 5th year	
055	Additional copy of docs cited in search report		036	Renewal fee for the 6th year	
015	Claims fee(s) (Rules 45(1), 162(1)EPC)[5]			Validation for[8]	
005	Designaton fee(s)[4]		037	Renewal fee for the 7th year	1,165.00
006	Examination fee				
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123	Fee for further processing (late payment of a fee)			Extension for[8]	
007	Fee for grant and printing or fee for grant incl. fee for publcation[6]				
008	Additional printing fee for 36th and each subsequent page[7]				
016	Claims fee according to Rule 71(6) EPC[5]				
121	Fee for further processing (late performance of acts R.71(3))				
022	Registering of transfer				

Notes 1 - 9 see overleaf.

Total 1,165.00

Signature (handwritten/no block letters)
Bailey Walsh + Co

Place, Date
Leeds, UK; 16 January 2017

EPO 1010 04.14

Bailey &

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M. Kellett, MITMA
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Yours faithfully
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036	Renewal fee for the 6th year	
	Validation for[9]	
037	Renewal fee for the 7th year	1,165.00
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Notes 1 - 9 see overleaf.

Total 1,165.00

EPO 1010 04.14

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Place, Date: Leeds, UK; 16 January 2017

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 115

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EP 14185786.2

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002	Fee for a European search		035	Renewal fee for the 5th year	
055	Additional copy of docs cited in search report		036	Renewal fee for the 6th year	
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022	Registering of transfer				

Notes 1 - 9 see overleaf.

Total: 1,165.00

Signature (handwritten/no block letters): Bailey Walsh + Co

Place, Date: Leeds, UK; 16 January 2017

EPO 1010 04.14

Bailey Walsh & Co

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M. Kellett, MITMA
D. Corbyn, MChem (Hons), CPA, EPA

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29.Nov. 2016

BY FACSIMILE

Confirmation only
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Our ref.: AT-X11031DIV2-EP
Your ref.: 8568/000030
25 November 2016

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Further to issuance of the Examination Report dated 29th September 2016, we respond as follows.

The examiner has indicated in their report that claim 3 in combination with claim 1 of the present application corresponds to claim 1 of European Patent 11861339 (EP2688399). We respectfully disagree with the examiner for the following reasons.

Claim 1 of the parent patent EP2688399 **does** include certain limitations of amended claims 1 and 3 of the present application, such as the weight percent of the sodium hydroxide of 1.82-7.28% and the mole ratio of 4.2:3.8:1. However, claim 1 of the parent patent EP2688399 **does not** include the step b) of "introducing triacetin and aqueous hydrogen peroxide to the water". Instead, the parent claim 1 has step b) of "introducing a hydrogen peroxide-triacetin solution to the water". This difference is significant.

Claim 1 of the parent patent requires the addition of **one component, a solution that contains both triacetin and hydrogen peroxide in it** to the water. Claim 1 of the

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presently amended application requires the addition of **two separate components, triacetin and hydrogen peroxide,** to the water. The two components do not have to be added as a single solution already mixed together, as the parent requires. This makes the claims of the presently amended application different, but also provides a simpler methodology. Thus, the claims of the present application and the claims of the parent granted patent do not result in double patenting and granted patents for each should be allowed.

We trust the above overcomes the objections by the examiner. In the event the examiner intends to reject the present application without providing the applicant with a further opportunity to respond in writing, we hereby request Oral Proceedings under Art. 116 EPC in respect of this matter.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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D. Corbyn, MChem (Hons), CPA, EPA

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25 November 2016

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Further to issuance of the Examination Report dated 29th September 2016, we respond as follows.

The examiner has indicated in their report that claim 3 in combination with claim 1 of the present application corresponds to claim 1 of European Patent 11861339 (EP2688399). We respectfully disagree with the examiner for the following reasons.

Claim 1 of the parent patent EP2688399 **does** include certain limitations of amended claims 1 and 3 of the present application, such as the weight percent of the sodium hydroxide of 1.82-7.28% and the mole ratio of 4.2:3.8:1. However, claim 1 of the parent patent EP2688399 **does not** include the step b) of "introducing triacetin and aqueous hydrogen peroxide to the water". Instead, the parent claim 1 has step b) of "introducing a hydrogen peroxide-triacetin solution to the water". This difference is significant.

Claim 1 of the parent patent requires the addition of **one component, a solution that contains both triacetin and hydrogen peroxide in it** to the water. Claim 1 of the

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presently amended application requires the addition of **two separate components, triacetin and hydrogen peroxide,** to the water. The two components do not have to be added as a single solution already mixed together, as the parent requires. This makes the claims of the presently amended application different, but also provides a simpler methodology. Thus, the claims of the present application and the claims of the parent granted patent do not result in double patenting and granted patents for each should be allowed.

We trust the above overcomes the objections by the examiner. In the event the examiner intends to reject the present application without providing the applicant with a further opportunity to respond in writing, we hereby request Oral Proceedings under Art. 116 EPC in respect of this matter.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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The examination is being carried out on the **following application documents**

Description, Pages

25-59	as originally filed			
1-24	received on	07-09-2015	with letter of	07-09-2015

Claims, Numbers

1-3	received on	07-09-2015	with letter of	07-09-2015

Drawings, Sheets

1/1	as originally filed

The attention of the applicant is drawn to the fact that claim 3 in combination with claim 1 corresponds to claim 1 of European Patent 11861339, already belonging to the applicant and granted on the 27.07.2015.

It is not clear which difference would make for the person skilled in the art to perform the process in the way it is described in claim 1 of EP11861339 or according to the present application as claimed in claim 3.

The EPO does not allow double patenting, basing this principle on the idea that the applicant has not legitimate interest in proceedings that gave rise to the grant of a second patent in respect of the same subject-matter for which he already holds one.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 121

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Application No.	Ref.	Date
14 185 786.2 - 1454	AT-BF-G49415	29.09.2016
Applicant Enviro Tech Chemical Services Inc.		

Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

of 2 months

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).

Registered letter

Petitioner's Exhibit 1022
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IPR2025-01471 – Page 122

Zanobini, Alessandra
Primary Examiner
For the Examining Division

Enclosure(s): 1 page/s reasons (Form 2906)

Registered letter
EPO Form 2001 12.10CSX

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Application No.: 14185786.2

Substantive examination has started on 31.08.16 (see Notice from the European Patent Office dated 29.01.2013, OJ EPO 2013, 153).

For the Examining Division

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 124

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D-80298 Munich
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BY FACSIMILE
00498923994465

Our ref: X11031DIV2-EP
19 January 2016

Dear Sirs

Re: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Would you please deduct **€1040.00** from our Account No. 28050202 in payment of the 6th annuity due on the above application before the end of March 2016.

Yours faithfully
BAILEY WALSH & CO. LLP
Baley walsh + Co

Zur Kasse
1.040,-

Also at 20 Bootham, York, YO30 7BL, UK **Tel:** 0800 783 7623
3M Buckley Innovation Centre, Firth Street, Huddersfield, HD1 3BD, UK **Tel:** 0800 783 7623
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Code		Amount/EUR
001	Filing fee – EP direct[3]	
501	Additional fee (more than 35 pages)	
020	Filing fee – entry EP phase[3] (Rule 159(1)(c) EPC)	
520	Additional fee (more than 35 pages) – entry EP phase	
	Additional fee for divisional applications (Rule 38(4)EPC)[9]	
002	Fee for a European search	
055	Additional copy of docs cited in search report	
015	Claims fee(s) (Rules 45(1), 162(1)EPC)[5]	
005	Designaton fee(s)[4]	
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121	Fee for further processing (late performance of acts R.71(3))	
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033	Renewal fee for the 3rd year	
034	Renewal fee for the 4th year	
035	Renewal fee for the 5th year	
036	Renewal fee for the 6th year	1,040.00
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Notes 1 - 9 see overleaf.

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Bailey Walsh + Co

Place, Date

Leeds, UK; 19 January 2016

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Dear Sirs

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Place, Date
Leeds, UK; 19 January 2016

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

~~2. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced simultaneously.~~

~~3. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced sequentially with either one first.~~

~~4. The method of claim 1, wherein the provided water is an aqueous stream.~~

~~5. The method of claim 1, wherein the provided water is contained in a mixing tank or other vessel.~~

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~~6. The method of claim 1, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.~~

~~7. The method of claim 6, wherein the sodium hydroxide is about 1.82% to about 7.28%.~~

~~8. The method of claim 1, wherein step (d) is performed simultaneously with step (b).~~

~~9~~2. The method of claim 1, further comprising allowing the reaction medium ~~sufficient time~~30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

~~10. The method of claim 9, wherein the time to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid is about 30 seconds to about five minutes.~~

~~11. The method of claim 10, wherein the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.~~

~~12~~3. The method of claim ~~6~~1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is ~~about~~ 4.2:3.8:1.

~~13. The method of claim 1, wherein said steps (a) through (e) are performed on a continuous basis.~~

~~14. The method of claim 1, wherein said steps (a) through (e) are performed on an intermittent basis.~~

FIELD OF THE INVENITON

[0001] The invention relates to liquid compositions and methods of using the liquid compositions for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. The invention also relates to a solid bleaching and stain removal composition.

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water (about 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generated in-situ. It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519

A1.This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generated in-situ in the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a method of generating a non-equilibrium solution of peracetic acid as defined by claim 1.

[0020] A further embodiment is a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be

contained in a mixing tank or other vessel.. The liquid acetyl precursor is triacetin. In accordance with the invention, the acetyl precursor and the aqueous hydrogen peroxide are introduced to the water separately, either sequentially, with either one first, or simultaneously.. The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within about 30 seconds to about five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. With triacetin used as the acetyl precursor and assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is about 0.078% to about 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of about 11.2 to about 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from about 1% to about 7.1%.

[0022] The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. The triacetin that is used as the acetyl precursor, is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[0026] The term "receiving water" means the water that is being treated.

[0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[0028] PAA and hydrogen peroxide in solution were determined using the ceric

sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate} \times 0.17}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate} \times 0.38}{\text{wt . sample}}$$

[0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[0030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD),

which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[0031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

3. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

[0035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[0036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate

should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[0037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[0041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at

which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[0042] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0043] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For example, with 3/4" pipe, a static mixer of 3/4" diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0044] An aqueous source of an alkali metal or earth alkali metal hydroxide is

provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0045] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. With the acetyl precursor as triacetin, a mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[0046] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0047] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[0048] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor

employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[0050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[0052] In another embodiment, a method of continuously or intermittently generating

a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0054] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[0056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either

simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. With the acetyl precursor as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[0061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[0064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$H_2O_2=H^+ + HO_2-$

[0066] The perhydroxyl anion (HO_2-) then affects nucleophilic substitution reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. With the acetyl precursor as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. With triacetin used, assuming all three acetyl groups are reacted,

about 40.9% to about 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is about 0.078% to about 1.88%.

[0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

[0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example 1

[0072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

Table VIII

t #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

Example 2

[0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to about 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of about 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

Example 3

[0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6

5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

FIELD OF THE INVENITON

[0001] The invention relates to liquid compositions and methods of using the liquid compositions for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. The invention also relates to a solid bleaching and stain removal composition.

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water (about 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generatedin-situ.It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519 A1.

This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generatedin-situin the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a method of generating a non-equilibrium solution of peracetic acid as defined by claim 1.

~~[0015] In an embodiment, liquid compositions for use in generating non-equilibrium solutions of PAA are provided. These hydrogen peroxide-acetyl precursor solutions comprise a solution of aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water. A~~

~~preferable acetyl precursor is triacetin, which displays an unexpectedly high solubility in hydrogen peroxide. These hydrogen peroxide acetyl precursor solutions may be used for generating a non-equilibrium solution of peracetic acid for use as a disinfectant or sanitizer on a site having a point-of-use of peracetic acid.~~

~~[0016] The hydrogen peroxide acetyl precursor solutions are advantageous in that they are formulated such that sufficient acetyl precursor can be dissolved in an amount of hydrogen peroxide that would fully perhydrolyze all of the acetyl groups of the acetyl precursor. Moverover, the hydrogen peroxide component of these compositions is remarkably stable. These compositions overcome one or more problems of the known prior art, and are free of the regulatory reporting, permitting, and shipping restrictions that govern equilibrium PAA products.~~

~~[0017] In another embodiment, a method of preparing a hydrogen peroxide acetyl precursor solution is provided. The method comprises introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide acetyl precursor solution.~~

[~~0018~~0020] A further embodiment is a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be contained in a mixing tank or other vessel. ~~A hydrogen peroxide acetyl precursor solution is provided on the site having the point-of-use~~. ~~In one embodiment, t~~The liquid acetyl precursor is triacetin. ~~and the solution that is formed is a hydrogen peroxide triacetin solution. The hydrogen peroxide acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and then used to prepare the hydrogen peroxide acetyl precursor solution on the site. The hydrogen peroxide acetyl precursor solution is then introduced to the water. Alternatively, and in~~In accordance with the invention ~~another embodiment~~, the acetyl precursor and the aqueous hydrogen peroxide ~~may be~~are introduced to the water separately, either sequentially, with either one first, or

simultaneously. ~~The hydrogen peroxide-acetyl precursor solution and the water are mixed to form a mixture~~. ~~An aqueous source of an alkali metal or earth alkali metal hydroxide, such as~~The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of ~~an alkali metal or earth alkali metal~~sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of ~~alkali metal or earth alkali metal~~sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within about 30 seconds to about five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. ~~When~~ With triacetin ~~is~~ used as the acetyl precursor and assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is about 0.078% to about 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of ~~alkali metal or earth alkali metal~~ sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[~~0019~~0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of about 11.2 to about 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from about 1% to about 7.1%.

[~~0020~~0022] ~~The PAA solution is introduced to the receiving water at the point-of-use. It may be introduced immediately, or stabilized with the addition of a source of acid and used throughout a working day.~~ The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat,

poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[~~0021~~0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. ~~When~~ The triacetin that is used as the acetyl precursor, ~~it~~ is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

~~[0022] In another embodiment, a freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided. The solid composition comprises a liquid acetyl precursor, a water soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. The liquid acetyl precursor is preferably triacetin The composition produces peracetic acid upon being introduced to water. Upon dissolution, the solid hydrogen peroxide source releases hydrogen peroxide and the solid source of alkalinity dissolves to increase the pH, resulting in the formation of peracetic acid from the reaction of the hydrogen peroxide and the acetyl precursor.~~

~~[0023] The solid composition is used as a bleaching agent and a stain remover for the treatment of articles such as fabrics, dentures, textile garments, and equipment used in the food and beverage industry. The solid composition is advantageous in that it does not give rise to an undesirable PAA odor upon storage, contains an acetyl precursor that efficiently utilizes the acetyl groups it contains, and has a high solubility in cool~~

~~temperature water which quickly and efficiently produces PAA without the need for elevated water temperatures. Moreover, the acetyl precursor used in making the solid composition may also be used in preparing the liquid compositions described in section 3 above, streamlining manufacturing practices by using the same acetyl precursor as an ingredient in liquid as well as solid compositions.~~

~~[0024] Surprisingly, this freely flowable, solid composition includes a liquid acetyl precursor, triacetin. In addition, it is surprising that this composition does not produce a strong odor of peracetic acid during storage.~~

~~[0025] In another embodiment, a method of preparing the freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided.~~

~~BRIEF DESCRIPTION OF THE DRAWING~~

~~[0026] Figure 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point of use of peracetic acid In another embodiment, a freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.~~

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[~~0027~~0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[~~0028~~0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[~~0029~~0026] The term "receiving water" means the water that is being treated.

[~~0030~~0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[~~0031~~0028] PAA and hydrogen peroxide in solution were determined using the ceric sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate x 0.17}}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate x 0.38}}{\text{wt . sample}}$$

[~~0032~~0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the

samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[~~0033~~0030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD), which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[~~0034~~0031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

~~3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA On a Site Having a Point-of Use~~

~~[0035] In an embodiment, liquid compositions for generating non-equilibrium solutions of PAA on a site having a point-of use of peracetic acid are provided. These solutions are referred to as "hydrogen peroxide-acetyl precursor solutions." These solutions comprise aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water.~~

~~[0036] The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.~~

~~(a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.~~

~~[0037] Triacetin is a preferable liquid acetyl precursor and 50% hydrogen peroxide is a preferable solution of aqueous hydrogen peroxide. The triacetin is preferably added to the 50% hydrogen peroxide at room temperature. Alternatively, 70% hydrogen peroxide can be used, but it is not widely available and requires special handling and transportation. Given that the solubility of triacetin in water is only 7% at 25°C, triacetin is unexpectedly highly soluble in 50% hydrogen peroxide. It solubilizes without an exotherm (temperature increase).~~

~~[0038] The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.~~

~~(b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.~~

~~[0039] The solution is mixed until a homogenous solution has been formed. The solution is allowed to mix by diffusion or by using a mixing device that is suitable for mixing liquids together. For example, 50% hydrogen peroxide can be introduced to a batch tank equipped with an overhead agitator blade. Triacetin can then be introduced to the 50% hydrogen peroxide when the agitator is in motion so that the components are thoroughly mixed.~~

~~[0040] The solution that is formed is a hydrogen peroxide-acetyl precursor solution, which also includes varying amounts of water, depending on the formulation used. When triacetin is used as the liquid acetyl precursor, the solution that is formed is a hydrogen peroxide-triacetin solution. One such hydrogen peroxide-triacetin solution comprises about 23% to about 40% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 20% to about 52% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor~~

solution. The pH is about 1.46 to about 2.2 and no deliberate attempt is made to adjust the pH further.

[0041] A preferable hydrogen peroxide-triacetin solution comprises about 27.15% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 45.67% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor solution. The mole ratio of hydrogen peroxide:triacetin is about 3.8:1.

[0042] The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

Example 1

[0043] Triacetin (83.05 g) was added to 50% hydrogen peroxide solution (75 g) to form 158.05 g of a mixture. There was no evolution of gas indicating the hydrogen peroxide had decomposed to oxygen, nor was there any exotherm indicating that a chemical reaction had occurred. The solution did not turn oily or cloudy but remained clear. The solution was calculated to comprise 23.73% hydrogen peroxide and 52.55% triacetin, with the balance being water, and had a measured pH of 2.2. The mole ratio of hydrogen peroxide to triacetin was calculated to be 2.98:1. Titration of the solution immediately upon preparation yielded 24.1% hydrogen peroxide, which is within experimental error of the calculated amount of hydrogen peroxide.

[0044] This experiment showed that triacetin is remarkably soluble in 50% hydrogen peroxide. The solubility of triacetin was found to be at least 52.55%. This is surprising, given that the solubility of triacetin in water is only 7% at 25°C.

[0045] In order to test the stability of the mixture, the amount of hydrogen peroxide remaining and the amount of PAA generated was tracked for several months. The

~~mixture was held at ambient temperature away from sources of light. Table I summarizes the data.~~

~~[0046] Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.~~

~~Example 2~~

~~[0047] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 12.84:1 was prepared by adding triacetin (100.0 g) to 50% hydrogen peroxide (400.0 g) so that the mixture was 40% hydrogen peroxide and 20% triacetin, with the balance being water. The pH of the solution was 1.46 and the pH of a 1:100 dilution was 3.69. To accelerate storage characteristics, the sample was placed in an incubator set for 86-87°F. Table II shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of more than six months.~~

[0048] Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

Example 3

[0049] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin (37.5008 g) to 50% hydrogen peroxide (65.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87°F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

Table III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

[0050] In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have

~~been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.~~

~~Example 4~~

~~[0051] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.~~

Table IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

~~[0052] Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.~~

~~Example 5~~

~~[0053] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 4.8:1 was prepared by adding triacetin (37.50 g) to 50% hydrogen peroxide (56.25 g) so that the mixture was 30% hydrogen peroxide and 40% triacetin, with the balance being water. The pH of the solution was 1.67 and the pH of a 1:100 dilution was 4.62. To accelerate degradation, the sample was placed in an incubator set for 86-87° F.~~

~~Table V shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 43 days.~~

Table V

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	30.08	0.38
8	29.85	0.784
15	29.63	1.22
22	29.37	1.71
29	28.76	2.26
36	28.67	2.78
43	28.31	3.41

~~[0054] Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.~~

~~Example 6~~

~~[0055] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.~~

Table VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

~~[0056] Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.~~

~~Example 7~~

~~[0057] A 30-gallon batch of 50% hydrogen peroxide and triacetin was prepared by blending 137 lbs triacetin with 163 lbs 50% hydrogen peroxide so that the mixture was 27.15% hydrogen peroxide and 45.67% triacetin, with the balance being water. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The mixture was stored in an opaque drum in a non-climate controlled environment. On storage, the mixture slowly formed PAA in the container. Since this reaction of hydrogen peroxide to PAA does not represent a destructive loss of total peroxygen, to determine the true stability of the hydrogen peroxide, both the hydrogen peroxide and the peracetic acid generated must be quantified and reported as total peroxygen recovered.~~

~~[0058] After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate-iodometric titration method, the PAA generated~~

~~and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.~~

Table VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

~~[0059] After 295 days, 22.17% of the total peroxygen was recovered as either titratable hydrogen peroxide or hydrogen peroxide reacted to form PAA. To determine the stability of the peroxygen in the mixture, the total recovered hydrogen peroxide after 295 days (22.17%) was subtracted from the total recovered hydrogen peroxide of the initial theoretical value (27.17%). The result, 5%, is the loss of peroxygen (expressed as hydrogen peroxide) after 295 days of storage in a non-climate controlled environment.~~

43. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[~~0060~~0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[~~0061~~0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

[~~0062~~0035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[~~0063~~0036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[~~0064~~0037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[~~0065~~0038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[~~0066~~0039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[~~0067~~0040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[~~0068~~0041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the

water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[~~0069~~0042] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[~~0070~~0043] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For

example, with 3/4" pipe, a static mixer of 3/4" diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[~~0071~~0044] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. ~~A preferable~~The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. ~~Other suitable alkali metal hydroxides include 45% potassium hydroxide .~~

[~~0072~~0045] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. ~~When~~ With the acetyl precursor ~~is~~ as triacetin, a ~~preferred~~ mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[~~0073~~0046] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[~~0074~~0047] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[~~0075~~0048] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[~~0076~~0049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[~~0077~~0050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. ~~When~~ With the acetyl precursors ~~is~~ as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[~~0078~~0051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the

highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[~~0079~~0052] In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

[0080] A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[~~0081~~0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[~~0082~~0054] ~~A preferable~~The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[~~0083~~0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[~~0084~~0056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[~~0085~~0057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially: If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[~~0086~~0058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[~~0087~~0059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. ~~A preferable~~The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. ~~Other suitable alkali metal hydroxides include 45% potassium hydroxide.~~

[~~0088~~0060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. ~~When~~ With the acetyl precursor ~~is~~ as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[~~0089~~0061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[~~0090~~0062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[~~0091~~0063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[~~0092~~0064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. ~~When~~ With the acetyl precursors ~~is~~ as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[~~0093~~0065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$H_2O_2=H^+ + HO_2-$

[~~0094~~0066] The perhydroxyl anion (HO_2-) then affects nucleophilic substitution

reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. ~~When~~ With the acetyl precursor ~~is~~ as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[~~0095~~0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. ~~When~~ With triacetin ~~is~~ used, assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is about 0.078% to about 1.88%.

[~~0096~~0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

[~~0097~~0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[~~0098~~0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[~~0099~~0071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example ~~8~~1

[~~0100~~0072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for

perhydrolysis.

Table VIII

it #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[~~0101~~0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

~~Example 9~~

~~[0102] A mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (63.4%) and triacetin (36.6%). Thus, the mole ratio of hydrogen peroxide:triacetin was 5.57:1. The mixture (13.68 g) was added to soft water such that the final solution contained 5 g/L of triacetin and had a pH of 4.1. Then, in successive experiments, sufficient 50% NaOH was added to the beaker so that the mole ratio of NaOH:TA was varied from 3:1 (obtained by introducing 5.49 g of 50% NaOH) to 8:1 (obtained by introducing 14.68 g of 50% NaOH). Using the ceric sulfate iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the 6:1 mole ratio of NaOH:TA are shown in Table IX.~~

Table IX

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
0	0.015	0.437	2.9
1	0.275	0.298	53.1
3	0.312	0.274	60.2
5	0.326	0.258	62.9
11	0.302	0.233	58.3
21	0.246	0.199	47.5

~~[0103] It can be seen that even before the introduction of 50% NaOH, some PAA was present in solution as a result of being generated in the diluted mixture of the two components. Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.326% occurring at five minutes, corresponding to a yield of 62.9% assuming all three acetyl groups of triacetin were available for perhydrolysis.~~

~~[0104] This exercise was repeated for mole ratios of NaOH: triacetin ranging from 3:1 to 8:1. Table X summarizes the next set of data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.~~

~~[0105] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.~~

Example ~~10~~2

[~~0106~~0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to about 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of about 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[~~0107~~0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[~~0108~~0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[~~0109~~0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

Example ~~11~~3

[~~01100~~0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6
5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[~~01110~~0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[~~01120~~0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the

calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[~~0113~~0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

~~Example 12~~

~~[0114] In the first test, a mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (54.24%) and triacetin (45.76%). Thus, the mole ratio of hydrogen peroxide:triacetin was 3.65:1. The mixture (51.22 g) was dissolved in soft water (911.9 g) in a one-liter beaker to yield a solution with a pH of 6.47. Then, 50% NaOH (36.47 g) was introduced with stirring. Thus, the mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin was 4.2:3.8:1. The pH of the resulting solution initially measured 12.1. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes. It was noticed that the sample temperature rose immediately upon addition of the 50% NaOH.~~

~~[0115] In the second test, the first test was repeated, except that the water was chilled soft water.~~

~~[0116] In the third test, the first test was repeated using three times the original amount of hydrogen peroxide:triacetin mixture and three times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (153.96 g) was introduced to chilled soft water (735.6 g) in a one liter beaker to yield a solution with an initial pH of 5.14. Then, 50% NaOH (111.21 g) was introduced. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.~~

~~[0117] In the fourth test, the first test was repeated using four times the original amount of hydrogen peroxide:triacetin mixture and four times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (204.7 g) was introduced to chilled soft water (647.5 g) in a one-liter beaker to yield a solution with an initial pH of 6.32. Then, 50% NaOH (155.4 g) was introduced. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.~~

~~[0118] Table XV summarizes the results obtained for the four tests and shows the initial and final solution temperatures, the pH of the solution after the addition of the 50% NaOH, the maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.~~

Table XV

Test #	Initial Temp. (°F)	Final Temp. (°F)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88
NM = not measured					

~~[0119] Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.~~

Table XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

~~[0120] The data in Tables XV and XVI indicate that far higher amounts of PAA are possible if the 50% sodium hydroxide solution is the last component of the mixture to be introduced. Further, up to 7.1% PAA was generated, although this solution got hot despite chilling the source water. Generation of the 6.3% PAA solution was very efficient because it represented a high 85.7% utilization of triacetin converted into PAA. There was clearly a linear relationship between Test 2, which generated 2.1% PAPA, and Test 3, which utilized three times more of the reactants and generated 6.3% PAA. The data in Table XV indicate that the time of maximum conversion of triacetin was between one and four minutes. Thereafter, the amount of PAA in solution is reduced because it undergoes high pH degradation slowly over the following 10 minutes.~~

~~Example 13~~

~~[0121] Fig. 1 is a schematic representation of an example of a system 10 that was used to perform an embodiment of one of the methods described above to prepare a non-equilibrium solution of PAA on a site having a point of use. Triacetin was used as the~~

~~acetyl precursor and 50% sodium hydroxide was used as the aqueous source of an alkali metal hydroxide.~~

~~[0122] A container 120 of a hydrogen peroxide-acetyl precursor solution, which was a hydrogen peroxide-triacetin solution, and a container 140 of 50% sodium hydroxide were each equipped with chemical delivery diaphragm pumps 115 and 135, respectively. Inlet water 90, which was softened, was provided from a water source on the site having the point-of-use. Inlet water 90 was directed through a pressure regulator 100 and flow meter 105, then into a section of pipe where the hydrogen peroxide-triacetin solution was introduced through injection quill 110. Mixing was accomplished using static mixer 125. Then, the sodium hydroxide solution was added through injection quill 130 to form a reaction medium.~~

~~[0123] The hydrogen peroxide-triacetin solution and the sodium hydroxide solution may be added in a sequential manner as described, where the hydrogen peroxide-triacetin solution was added first, or they may be added to the water simultaneously through a "T" fitting placed before static mixer 125. If a T fitting is used, the hydrogen peroxide- triacetin solution and the 50% sodium hydroxide solution are introduced to opposite ends of the T fitting and the mixture is injected into the pipe of water. In other embodiments, the hydrogen peroxide and triacetin may be added separately, or sequentially, with either one first, or simultaneously, with the sodium hydroxide added either simultaneously with, or after, the hydrogen peroxide and triacetin.~~

~~[0124] The reaction medium was introduced to a residence chamber 145 which provided reaction time and contained a packing material to promote mixing. Residence chamber 145 was designed to be of a volume such that at a total flow rate of one gallon per minute, by the time the reaction medium reached sampling port 160, 30 seconds had elapsed since the sodium hydroxide solution had been added. A pH probe 155 monitored the pH of the mixture.~~

~~[0125] A controller 150 was interfaced to the flow meter 105 of the inlet water 90, and also to the chemical delivery diaphragm pumps 115 and 135. The controller 150 monitored the rate of the inlet water 90 and governed the rate at which the hydrogen~~

peroxide-triacetin solution and the NaOH solution were introduced. If the flow of inlet water 90 decreased because of lower PAA requirements at the point-of-use 195, the rates at which the hydrogen peroxide-triacetin solution and the NaOH solution were pumped decreased accordingly. If the flow of inlet water 90 increased because of higher PAA requirements at the point-of-use 195, the rates at which the hydrogen peroxide-triacetin solution and the NaOH solution were pumped increased accordingly. If the flow of inlet water 90 stopped, pumps 115 and 135 stopped. Thus, the generation of PAA was both continuous and intermittent, and was tailored to the PAA requirements at the point-of-use.

[0126] The rate of the reaction between the hydrogen peroxide and the triacetin to form PAA is dependent upon the temperature of inlet water 90. If the temperature of inlet water 90 is high (for example, about 70°F), the maximum conversion of triacetin into PAA may occur after 30 seconds, in which case the entire reaction medium was directed to the point-of-use 195. However, if the temperature of inlet water 90 is low (for example, about 32°F), longer reaction times may be necessary to maximize the conversion of triacetin into PAA. Then, the reaction medium was directed through one or more residence chambers 165, 175, and 185 which also contained a packing material to promote turbulence and cause thorough mixing. Residence chambers 165, 175, and 185 were designed to be of volumes such that at a total flow rate of one gallon per minute, the reaction medium reached sampling port 170 in one minute, sampling port 180 in two minutes, and sampling port 190 in five minutes, to permit sampling at different time intervals.

[0127] Thus, depending on the temperature of the inlet water, the time to achieve the maximum conversion of hydrogen peroxide and triacetin into PAA was determined by sampling and analyzing the solution at sample ports 160, 170, 180, and 190. The entire flow was then directed from the sampling port with the highest amount of PAA to the point-of-use 195. In practice, the PAA generated from the reaction of hydrogen peroxide with triacetin is typically diluted at the point-of-use 195.

[0128] Point-of-use 195 may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products;

fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

Example 14

[0129] Referring again to Fig. 1 , a 55-gallon drum container 120 of a hydrogen peroxide-triacetin solution was prepared by mixing triacetin (251.5 lbs) with 50% hydrogen peroxide (298.4 lbs). The resulting 550 lbs of hydrogen peroxide-triacetin solution had a specific gravity of 1.19 g/mL (10 lbs/gal) and contained 54.3% hydrogen peroxide and 45.7% triacetin. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The apparatus depicted in Fig. 1 was used to continuously and intermittently prepare an approximately 1% PAA solution.

[0130] Softened local city water was directed through pressure regulator 100 at a flow rate of one gallon per minute as measured by flow meter 105. The container 120 of hydrogen peroxide-triacetin solution was equipped with a draw down tube so that the flow rate of the mixture could be measured. Diaphragm pump 115 injected the hydrogen peroxide-triacetin solution through injection quill 110. The hydrogen peroxide-triacetin solution was then mixed with the softened water using static mixer 125. A container 140 of 50% NaOH was also equipped with a draw down tube to measure the flow pumped by diaphragm pump 135 into injection quill 130.

[0131] The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate-iodometric titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

Table XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide—Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	~13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37

4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

[0132] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing flow rate of NaOH. For this mole ratio of hydrogen peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

Example 15

[0133] E. coliO157:H7 bacteria (ATCC 35150) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one-liter test solutions.

[0134] Salmonella typhimurium bacteria (ATCC 14028) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one-liter test solutions.

[0135] The amount of E. coliO157:H7 and Salmonella typhimuriumbacteria were measured by serial dilution and plating on 3ME. coliplates and 3MEnterobacteriaceaePetrifilms, respectively.

[0136] A 1000 ppm stock of PAA was made by weighing 0.6386 g of Perasan MP-2 (5.83% hydrogen peroxide and 15.66% PAA) and adding water up to 100 g. Perasan MP-2 is an equilibrium product of PAA (Enviro Tech Chemical Services, Inc., Modesto, California). Side-by-side, one of theE. coliand one of theSalmonellatest

solutions were treated with a nominal dose of 1.0 ppm PAA by adding one mL of the 1000 ppm PAA stock solution to each sample. After one minute, approximately 100 mL of each test solution was removed, and sodium thiosulfate (0.5 g) was added to neutralize the PAA and hydrogen peroxide oxidants. After five minutes, sodium thiosulfate (0.5 g) was added to the remaining test solution to neutralize the PAA and hydrogen peroxide in the rest of the test solutions. The amount of viableE. coliO157:H7 andSalmonella typhimuriumbacteria remaining in the test solutions at the one-minute and five-minute contact times were measured by serial dilution and plating on 3ME. ColiPetrifilms and 3MEnterobacteriaceaePetrifilms, respectively.

[0137] A 1% solution of PAA was prepared by combining 30.90 g of a mixture of 50% hydrogen peroxide and triacetin (54.22% hydrogen peroxide and 45.78% triacetin) with 929.4 g of water, and then adding 50% NaOH (40.53 g). The PAA solution had a pH of 12.79. The mole ratio of this mixture was 3.8:7.8:1 NaOH:hydrogen peroxide:triacetin. One minute after preparation, the second one-liter E. Coli solution and the second one-liter Salmonella solution were treated with a nominal dose of 1.0 ppm PAA by adding 0.10 g of the 1% PAA solution to each sample. The test solution contact times, neutralization, and plating procedures were replicated for those that employed PAA from Perasan MP-2.

[0138] All 3ME. Coli Pertrifilms and 3MEnterobacteriaceaePetrifilms were incubated at 35°C for 24 hours. After incubation, the plates were enumerated.

[0139] Table XVIII shows the microbiological results of theE. coliO157:H7 test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. TheE. colitest solution started with log106.99 CFU/mL prior to being treated with 1.0 ppm of PAA from Perasan MP-2 or with 1 ppm of PAA from the 1% PAA solution.

[0140] TheE. colitest solution treated with 1.0 ppm PAA from Perasan MP-2 contained a log106.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log106.34 CFU/mL remained (77.50% reduction). The E. coli solution treated with a nominal 1.0 ppm PAA from the 1% PAA solution

~~contained a log106.78 CFU/mL after one minute and 6.63 CFU/mL after five minutes, respectively, corresponding to 38.02% and 56.12% reductions, respectively.~~

Table XVIII

E. coli O157:H7			
Description	log_{10} CFU/ml remaining	log_{10} reduction	% reduction
Control	6.99	N/A	N/A
Perasan MP-2 (1 min)	6.74	0.25	43.48
Perasan MP-2 (5 min)	6.34	0.65	77.50
1% PAA solution (1 min)	6.78	0.21	38.02
1% PAA solution (5 min)	6.63	0.36	56.12

~~[0141] Table XIX shows the microbiological results of the Salmonella typhimurium test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. The Salmonella test solution started with log107.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.~~

~~[0142] The Salmonella solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log101.76 CFU/mL after one minute and 0.70 CFU/mL after five minutes, corresponding to >99.999% reduction at both contact times. The Salmonella test solution treated with 1.0 ppm PAA from the 1% PAA solution contained a log106.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log104.95 CFU/mL remained (99.24% reduction).~~

Table XIX

Salmonella typhimurium			
Description	log_{10} CFU/ml remaining	log_{10} reduction	% reduction
Control	7.07	N/A	N/A
Perasan MP-2 (1 min)	1.76	5.31	99.9995
Perasan MP-2 (5 min)	0.70	6.37	>99.9999
1% PAA solution (1 min)	6.69	0.38	58.31
1% PAA solution (5 min)	4.95	2.12	99.24

~~[0143] The data in tables XVIII and XIX demonstrate that the 1 % PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%,~~

about equal to that of the Perasan MP-2, which was > 99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

[0144] A freely flowable, solid peroxygen bleaching and stain removal composition comprises a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. A preferable liquid acetyl precursor is triacetin. The water soluble solid source of hydrogen peroxide is preferably sodium percarbonate, although sodium perborate monohydrate or sodium perborate tetrahydrate may be used. The water-soluble solid source of alkalinity acts as a pH control agent, and may be an alkali metal or earth alkali metal bicarbonate, carbonate, sesquicarbonate, borate, silicate, or hydroxide. Examples include sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, sodium borate, sodium borate decahydrate (borax), sodium metasilicate, and sodium hydroxide.

[0145] In an embodiment, the composition comprises about 0.99% to about 8.45% triacetin, about 13% to about 54% sodium percarbonate, and about 24% to about 44% solid source of alkalinity.

[0146] The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispereency, and lower surface tension.

[0147] Metal ions present in the bleaching medium can have a tendency to deposit on the substrates being bleached. Therefore, the solid bleaching composition may optionally contain a metal chelating agent such as a polyacrylate, a phosphonate, a maleic acid, a salt of ethylenediaminetetraacetic acid, a salt of nitrilotriacetic acid, or a salt of gluconic acid.

[0148] Surfactants reduce the surface tension of the bleaching medium and enhance the process of cleaning the soiled article. Surfactants also disperse the soil particles removed from the article and keep them suspended. Therefore, the solid bleaching

~~composition may optionally contain a surfactant, such as an anionic, cationic, amphoteric, or non-ionic surfactant.~~

~~[0149] The solid bleaching composition may also optionally contain a solid zeolite, such as sodium zeolite, which acts to capture calcium and magnesium ions that may be present in the bleaching medium that would otherwise interact with an anionic surfactant, causing the surfactant to precipitate and removing it from the bleaching medium.~~

~~[0150] The composition may also optionally contain an inert, solid filler, such as anhydrous sodium sulfate, sodium sulfate decahydrate, or sodium chloride. The filler increases the total ionic strength of the aqueous phase, but imparts no chemical properties to the bleaching medium.~~

~~[0151] To make the solid peroxygen bleaching and stain removal composition, the water soluble solid source of hydrogen peroxide, the water-soluble solid source of alkalinity, any chelating agent, any sufactant, and any filler are blended with the liquid triacetin to form a solid bleaching composition. The components may be added in any order. Any blending equipment may be used. Suitable examples of equipment include a ribbon and paddle blender, a V and double cone blender, a Nauta screw mixer, and a rotating cement mixer. Alternatively, the ingredients may be blended by milling using a pulveriser mill, a ball mill, a hammer mill, a pin mill, an air mill, or a roller mill. Blending is performed for sufficient time to create a homongenous mixture. The mixture is a freely flowable solid which is readily discharged from the blender.~~

~~Example 16~~

~~[0152] A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.~~

Table XX

Component	%
Sodium carbonate, anhydrous	26.3
~~Sodium percarbonate~~	~~58.9~~
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

~~[0153] This solid peroxygen bleach precursor was then blended with incrementally increasing amounts of liquid triacetin. At each addition, the product was examined for flowability and for the odor of PAA. Table XXI summarizes the findings when up to 9.1g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.~~

Table XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely- flowable solid	None
2	Freely- flowable solid	None
~~3~~	~~Freely- flowable solid~~	~~None~~
4	Freely- flowable solid	None
5	Freely- flowable solid	None
6	Freely- flowable solid	None
7	Freely- flowable solid	None
~~8~~	~~Freely- flowable solid~~	~~None~~
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

~~[0154] Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45g of the triacetin to form a freely-flowable solid composition, without becoming a sticky, non-flowable product which would not pour easily or would become a solid mass upon storage inside a container.~~

~~[0155] The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.~~

Table XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

~~[0156] Another unexpected result was that after storing the composition for over one year at ambient temperature, the composition still had not developed an odor of PAA.~~

~~[0157] These surprising results are in contrast to the current belief that a liquid acetyl precursor, such as triacetin, could not be utilized with a solid source of hydrogen peroxide in a non-chlorine peroxygen bleaching and stain removal composition, for at least two reasons. First, when a non-chlorine peroxygen bleaching composition is used in residential and commercial laundering applications, the product must be a freely flowable solid. Typically, the acetyl precursor in a non-chlorinated peroxygen bleach is present in amounts up to 10%. It was believed that blending a liquid at this level with the other dry components of the laundry bleach would create a sticky, clumping mass, rather than a freely flowable solid, and would therefore not be acceptable to the user. Second, it was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.~~

~~Example 17~~

~~[0158] Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.~~

Table XXIII

Components of Composition A	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	41	615

(continued)

Components of Composition A	%	Charge Weights, g
Premix 1		
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	4	60
Soda Ash	16	240
Components of Composition B	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	43	645
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	2	30
Soda Ash	16	240

~~[0159] In both cases, Premix 1 was prepared by kneading the NANSA HS 90 (a sodium dodecylbenzenesulfonate surfactant) with the sodium sulfate. The sodium sulfate helped break up the sticky surfactant efficiently. Then, the sodium percarbonate, the sodium metasilicate, and the triacetin were added and mixed by hand.~~

~~[0160] In both cases, Premix 2 was prepared by mixing the sodium hydroxide beads with the mineral oil to afford a well-coated mixture, with some free-standing mineral oil remaining. Soda ash was blended in portions to take up the excess liquid and to provide a free-flowing solid mixture.~~

~~[0161] Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.~~

~~[0162] Both compositions A and B, which were held in uncovered bowls at ambient temperature after preparation, exhibited slow weight gain over time, most likely due to absorbance of water from the air. Each composition had gained 2.4% of its initial weight over a period of three days.~~

~~[0163] Neither composition exhibited significant exothermic behavior. However, composition A was hotter at the end of preparation and cooled more slowly than composition B. The temperature of composition A was 85°F immediately after preparation, rose to 88°F over the next ten minutes, and then fell slowly to 74°F. The temperature of composition B was 80°F immediately after preparation, rose to 81°F over the next twenty minutes, and then fell slowly to 65 °F.~~

~~[0164] The solid peroxygen bleaching and stain removal composition described above may be used as follows.~~

~~[0165] First, the solid peroxygen, composition is introduced to an aqueous medium that is used for bleaching or stain removal of at least one article contained within the aqueous medium. For bleaching of laundry articles, about 5g of bleaching composition is introduced for every liter of water used in the bleaching cycle. For home use, the bleaching composition can be added manually at the start of the wash.~~

For commercial laundry systems, the bleaching composition may be introduced just before the bleaching cycle, toward the end of the wash and following the soil removal cycle. In most commercial and residential laundry machines, bleaching cycles are typically about 10-15 minutes.

[0166] Second, the composition is allowed to dissolve and react to form the bleaching medium containing PAA. The solid source of hydrogen peroxide, such as sodium percarbonate, and the solid source of alkalinity, such as sodium hydroxide, dissolve in the laundry water and cause the pH of the water to increase to above about 10.5.

[0167] While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation: H2O2= H <+>+ HO2<->

[0168] The perhydroxyl anion (HO2<->) then effects nucleophilic substitution reactions on the carbonyl groups of triacetin, in a perhydrolysis reaction, to form PAA and 1,2,3-propanetriol (glycerine). The laundry water would also contain unreacted hydrogen peroxide, unreacted triacetin, and sodium hydroxide.

[0169] Third, the aqueous solution of PAA and the unreacted hydrogen peroxide are mixed for sufficient time to effect bleaching or stain removal of the articles contained within the aqueous medium. Both commercial and residential bleaching cycles are about 10-15 minutes.

[0170] Fourth, the article is rinsed with fresh water so that it becomes substantially free of PAA and the unreacted hydrogen peroxide, the glycerine, the unreacted triacetin, and the sodium hydroxide. Generally, for a laundered article, the washing machine is programmed to empty the bleaching medium and replace it with fresh water. The machine can agitate the articles with the rinse water to enhance the rinsing process.

[0171] Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically

dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally applied heat.

Example 18

[0172] Laundry swatches were made by cutting a tea towel into 50 equal 5 x 4 inch sheets. They were then separated into seven groups of seven swatches. Six of the groups were stained and the seventh group was left unstained for comparison purposes. Five of the groups that were stained were stained by soaking them in one of the following: black tea, black coffee, red wine, blood (pork), and acetone-extracted chlorophyll. The sixth group of swatches was stained by rubbing them on green grass. After allowing the stained swatches to dry, and before challenging the stains, the swatches were set aside for two months to allow the stains to set in the fabric.

[0173] A solid peroxygen bleaching and stain removal composition (200 g) was prepared by blending sodium percarbonate (104.0 g), triacetin (8.00 g), soda ash (80.01 g), and sodium hydroxide beads (8.00 g). The final product was a freely-flowable solid.

[0174] The composition was tested using 1:100 dilution at both 75°F and 104°F. The initial pH was measured and the concentrations of PAA and hydrogen peroxide were evaluated using the method of U.S. patent no. 7,651,724 . At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75°F, the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104°F had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H2O2). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75°F at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104°F at a pH of 11.2.

Table XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

Table XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426

(continued)

Time (min)	ppm PAA	ppm Hydrogen Peroxide
5.5	133	1494
7.8	122	1427
10.3	119	1405

~~[0175] The stain removal ability of the composition was determined by comparing treated swatches to control swatches (swatches washed in just city water for the same amount of time and at elevated temperature) and non-stained swatches. The description of the swatches is set forth in Table XXVI. Three stained swatches were used for each test. The composition (10.0 g) was weighed into a beaker (2000 mL). To this beaker a measured amount of hard water (990.0 g) was added at ambient~~

temperature (64°F). The swatches were added to the solution and agitated by mixing with a plastic utensil for 10 minutes to simulate a laundry bleaching cycle. After 10 minutes, the wash water was discarded and a water rinse was performed by adding fresh city water (1000.0 g) to the swatches and agitating for two minutes using the same plastic utensil. The swatches were immediately removed from the beaker after rinsing, wrung out by hand, and laid to dry. These steps were then repeated using water at an elevated temperature (120°F).

[0176] A control swatch was obtained by taking one swatch at a time from each stain group and washing in city water at an elevated temperature (120°F) for 10 minutes in the same manner as the treated swatches. After the wash, the swatches were immediately removed, wrung out by hand, and laid to dry.

Table XXVI

Type of Swatches	Description
Treated Swatches	Swatches subjected to bleaching for 10 minutes using bleaching formulation with triacetin and a 2-minute rinse with hard water
Control Swatches	Swatches subjected to only an elevated temperature (120°F) hard water wash for 10 minutes
Non-Stained Swatches	Non-altered swatches

[0177] The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

Table XXVII

Type of Stain	Bleaching Formula at 64°F	Bleaching Formula at 120°F
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

~~[0178] It can be seen that, in general, the composition displayed enhanced stain removal properties at elevated temperature. Excellent stain removal properties were obtained for black tea and black coffee, and more moderate performance with red wine and blood. The composition had virtually no effect on grass stains or the chlorophyll pigment that was acetone extracted from green grass.~~

~~[0179] The invention has been described above with the reference to the preferred embodiments. Those skilled in the art may envision other embodiments and variations of the invention that fall within the scope of the claims.~~

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07. Sep. 2015

BY FACSIMILE

Our ref.: AT-X11031DIV2-EP
Your ref.: 8658/17669P
02 Sept 2015

Confirmation only already sent by fax

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Further to issuance of the communication under Rule 70(2) and 70a(2) EPC dated 9th March 2015 and the extended European Search Report, please find enclosed amended pages of the application, together with a marked up version of the pages as amended and an indication below as to the amendments that have been made.

Claim Amendments

Claim 1 has been amended to include the subject matter of previous claims 6 and 7 of the application.

Previous claims 2-8 of the application have been deleted.

Previous claim 9 (now claim 2) has been amended to remove the wording "sufficient time" and to introduce the time period of previous claim 10.

Previous claims 10, 11, 13-14 of the application have been deleted.

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Previous claim 12 (now claim 3) has been amended to remove the word "about".

Objections in the Search Report

With regard to point 1 of the Search Report, claim 1 of the granted parent patent requires the feature of introducing a hydrogen peroxide-triacetin solution to water and the mole ratio of the three compounds. Newly amended claim 1 of the present application requires introducing the triacetin and hydrogen peroxide to water, as two separate components and not a single mixture of triacetin and hydrogen peroxide. Newly amended claim 1 does not include the mole ratio of the three compounds.

With regard to point 2 of the Search Report, the words "about" and "sufficient time" have been deleted from the claims. The system units for the sodium hydroxide have been included in amended claim 1. Previous claims 9 and 10 have been combined to form newly amended claim 2 which is no longer defined in terms of a result to be achieved. Previous claims 11, 13-14 have been deleted.

With regard to points 3 and 4 of the Search Report, claim 1 of the application has been amended to include the subject matter of previous claims 6 and 7. The examiner has already indicated that the subject matter of previous claim 7 is novel and inventive over the cited prior art.

With regard to point 5 of the Search Report, reference to D1-D4 has been made on page 7 of the present application. Reference to D5 is already provided on pages 5-6 of the application.

The description of the application has been brought into conformity with the amended claims.

We trust the above amendments are now sufficient to place the application in order for grant and we look forward to receiving confirmation to this effect in due course. In the event the examiner intends to reject the present application without providing the applicant with one or more opportunities for responding to the objections in writing, we hereby request Oral Proceedings under Art. 116 EPC in respect of this matter.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

2. The method of claim 1, further comprising allowing the reaction medium 30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

3. The method of claim 1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is 4.2:3.8:1.

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CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid, characterized in that the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide at 1.82% to 7.28% by weight.

~~2. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced simultaneously.~~

~~3. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced sequentially with either one first.~~

~~4. The method of claim 1, wherein the provided water is an aqueous stream.~~

~~5. The method of claim 1, wherein the provided water is contained in a mixing tank or other vessel.~~

2. Sep. 2015 15:12 bailey walsh & co No. 5876 P. 59
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~~6. The method of claim 1, wherein the aqueous source of the alkali metal or earth-alkali metal hydroxide is sodium hydroxide.~~

~~7. The method of claim 6, wherein the sodium hydroxide is about 1.82% to about 7.28%.~~

~~8. The method of claim 1, wherein step (d) is performed simultaneously with step (b).~~

92. The method of claim 1, further comprising allowing the reaction medium ~~sufficient time~~30 seconds to five minutes to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

~~10. The method of claim 9, wherein the time to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid is about 30 seconds to about five minutes.~~

~~11. The method of claim 10, wherein the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.~~

~~12~~3. The method of claim ~~6~~1, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is ~~about~~ 4.2:3.8:1.

~~13. The method of claim 1, wherein said steps (a) through (e) are performed on a continuous basis.~~

2. Sep. 2015 15:12 bailey walsh & co No. 5876 P. 60
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~~14. The method of claim 1, wherein said steps (a) through (e) are performed on an intermittent basis.~~

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FIELD OF THE INVENITON

[0001] The invention relates to liquid compositions and methods of using the liquid compositions for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. The invention also relates to a solid bleaching and stain removal composition.

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

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the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

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equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water (about 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

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compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

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1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generated in-situ. It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519

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A1.This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generated in-situ in the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

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fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a method of generating a non-equilibrium solution of peracetic acid as defined by claim 1.

[0020] A further embodiment is a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be

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contained in a mixing tank or other vessel.. The liquid acetyl precursor is triacetin. In accordance with the invention, the acetyl precursor and the aqueous hydrogen peroxide are introduced to the water separately, either sequentially, with either one first, or simultaneously.. The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within about 30 seconds to about five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. With triacetin used as the acetyl precursor and assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is about 0.078% to about 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of about 11.2 to about 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from about 1% to about 7.1%.

[0022] The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

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[0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. The triacetin that is used as the acetyl precursor, is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[0026] The term "receiving water" means the water that is being treated.

[0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[0028] PAA and hydrogen peroxide in solution were determined using the ceric

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sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate x 0.17}}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate x 0.38}}{\text{wt . sample}}$$

[0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[0030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD),

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which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[0031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

3. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

[0035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[0036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate

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should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[0037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[0041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at

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which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[0042] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0043] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For example, with 3/4" pipe, a static mixer of 3/4" diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0044] An aqueous source of an alkali metal or earth alkali metal hydroxide is

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provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0045] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. With the acetyl precursor as triacetin, a mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[0046] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0047] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[0048] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor

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employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[0050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[0052] In another embodiment, a method of continuously or intermittently generating

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a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0054] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[0056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either

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simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable.

[0060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. With the acetyl precursor as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[0061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

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(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[0063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[0064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. With the acetyl precursors as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[0065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$H_2O_2=H^+ + HO_2-$

[0066] The perhydroxyl anion (HO_2-) then affects nucleophilic substitution reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. With the acetyl precursor as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. With triacetin used, assuming all three acetyl groups are reacted,

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about 40.9% to about 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is about 0.078% to about 1.88%.

[0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

[0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example 1

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[0072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

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Table VIII

Exp. #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

Example 2

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[0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to about 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of about 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

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Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

Example 3

[0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6

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5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

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FIELD OF THE INVENITON

[0001] The invention relates to liquid compositions and methods of using the liquid compositions for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. The invention also relates to a solid bleaching and stain removal composition.

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

[0002] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0003] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0004] There are several problems with the use of equilibrium solutions of PAA. First,

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the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0005] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the

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equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0006] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0007] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988 , and U.S. Patent Application Publication No. 2009/0314652 . These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water (about 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode

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compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0008] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832 , These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0009] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538 . A solution containing a

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1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538 patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0010] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0011] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132 . This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generatedin-situ.It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

[0012] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519 A1,

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This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetra-acetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0013] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

B. Solid PAA Bleaches and Stain Removers

[0014] PAA is also used in laundry bleaching applications where it is generatedin-situin the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on

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fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

[0015] EP1618786 discloses a process for the production of a bactericide based on an organic peracid. The sterilising agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two components is 1/10 and 20/1.

[0016] JP2004230323 discloses a sterilising agent for hard surfaces. Triacetin is used as an agent capable of liberating acetic acid, hydrogen peroxide is added and a metal hydroxide is used to being the pH to 8-12.

[0017] US2010/227000 discloses a system for the preparation of a disinfectant of the peracetic acid type. A solid part A that is an acetyl source is combined with a liquid part B comprising 3-35% of hydrogen peroxide. A water solution of 0.05 to 5% alkali is added by adding sodium hydroxide. The pH is maintained between 5-8.

[0018] US6221341 discloses a tooth whitening composition. Peracetic acid is used as the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH.

SUMMARY OF THE INVENTION

[0019] The present invention relates to a method of generating a non-equilibrium solution of peracetic acid as defined by claim 1.

~~[0015] In an embodiment, liquid compositions for use in generating non-equilibrium solutions of PAA are provided. These hydrogen peroxide-acetyl precursor solutions comprise a solution of aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water. A~~

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~~preferable acetyl precursor is triacetin, which displays an unexpectedly high solubility in hydrogen peroxide. These hydrogen peroxide-acetyl precursor solutions may be used for generating a non-equilibrium solution of peracetic acid for use as a disinfectant or sanitizer on a site having a point-of use of peracetic acid.~~

~~[0016] The hydrogen peroxide-acetyl precursor solutions are advantageous in that they are formulated such that sufficient acetyl precursor can be dissolved in an amount of hydrogen peroxide that would fully perhydrolyze all of the acetyl groups of the acetyl precursor. Moreover, the hydrogen peroxide component of these compositions is remarkably stable. These compositions overcome one or more problems of the known prior art, and are free of the regulatory reporting, permitting, and shipping restrictions that govern equilibrium PAA products.~~

~~[0017] In another embodiment, a method of preparing a hydrogen peroxide-acetyl precursor solution is provided. The method comprises introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.~~

[~~0018~~0020] A further embodiment is a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be contained in a mixing tank or other vessel. ~~A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of use. In one embodiment, t~~The liquid acetyl precursor is triacetin. ~~and the solution that is formed is a hydrogen peroxide-triacetin solution. The hydrogen peroxide-acetyl precursor solution may be prepared off-site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and then used to prepare the hydrogen peroxide-acetyl precursor solution on the site. The hydrogen peroxide-acetyl precursor solution is then introduced to the water. Alternatively, and in~~In accordance with the invention ~~another embodiment~~, the acetyl precursor and the aqueous hydrogen peroxide ~~may be~~are introduced to the water separately, either sequentially, with either one first, or

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simultaneously. ~~The hydrogen peroxide acetyl precursor solution and the water are mixed to form a mixture~~. ~~An aqueous source of an alkali metal or earth alkali metal hydroxide, such as~~The sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of ~~an alkali metal or earth alkali metal~~sodium hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of ~~alkali metal or earth alkali metal~~sodium hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within about 30 seconds to about five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. ~~When~~ With triacetin ~~is~~ used as the acetyl precursor and assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is about 0.078% to about 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of ~~alkali metal or earth alkali metal~~ sodium hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[~~0019~~0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of about 11.2 to about 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from about 1% to about 7.1%.

[~~0020~~0022] ~~The PAA solution is introduced to the receiving water at the point-of-use. It may be introduced immediately, or stabilized with the addition of a source of acid and used throughout a working day.~~ The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat,

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poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[~~0021~~0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. ~~When~~ The triacetin that is used as the acetyl precursor, ~~it~~ is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

~~[0022] In another embodiment, a freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided. The solid composition comprises a liquid acetyl precursor, a water soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. The liquid acetyl precursor is preferably triacetin. The composition produces peracetic acid upon being introduced to water. Upon dissolution, the solid hydrogen peroxide source releases hydrogen peroxide and the solid source of alkalinity dissolves to increase the pH, resulting in the formation of peracetic acid from the reaction of the hydrogen peroxide and the acetyl precursor.~~

~~[0023] The solid composition is used as a bleaching agent and a stain remover for the treatment of articles such as fabrics, dentures, textile garments, and equipment used in the food and beverage industry. The solid composition is advantageous in that it does not give rise to an undesirable PAA odor upon storage, contains an acetyl precursor that efficiently utilizes the acetyl groups it contains, and has a high solubility in cool~~

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~~temperature water which quickly and efficiently produces PAA without the need for elevated water temperatures. Moreover, the acetyl precursor used in making the solid composition may also be used in preparing the liquid compositions described in section 3 above, streamlining manufacturing practices by using the same acetyl precursor as an ingredient in liquid as well as solid compositions.~~

~~[0024] Surprisingly, this freely flowable, solid composition includes a liquid acetyl precursor, triacetin. In addition, it is surprising that this composition does not produce a strong odor of peracetic acid during storage.~~

~~[0025] In another embodiment, a method of preparing the freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided.~~

~~BRIEF DESCRIPTION OF THE DRAWING~~

~~[0026] Figure 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point of use of peracetic acid In another embodiment, a freely flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.~~

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[~~0027~~0024] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[~~0028~~0025] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[~~0029~~0026] The term "receiving water" means the water that is being treated.

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[0030~~0~~0027] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

2. Experimental Methods

[0031~~0~~0028] PAA and hydrogen peroxide in solution were determined using the ceric sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate x 0.17}}{\text{wt . sample}}$$

$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate x 0.38}}{\text{wt . sample}}$$

[0032~~0~~0029] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the

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samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[00330030] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-p-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I<->) into iodine (I2) that reacts with a color indicator (DPD), which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2(76/71 = 1.07).

[00340031] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^+ ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2(34/71 = 0.479).

~~3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA On a Site Having a Point of Use~~

~~[0035] In an embodiment, liquid compositions for generating non-equilibrium solutions of PAA on a site having a point of use of peracetic acid are provided. These solutions are referred to as "hydrogen peroxide acetyl precursor solutions." These solutions comprise aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water.~~

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[0036] The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

(a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.

[0037] Triacetin is a preferable liquid acetyl precursor and 50% hydrogen peroxide is a preferable solution of aqueous hydrogen peroxide. The triacetin is preferably added to the 50% hydrogen peroxide at room temperature. Alternatively, 70% hydrogen peroxide can be used, but it is not widely available and requires special handling and transportation. Given that the solubility of triacetin in water is only 7% at 25°C, triacetin is unexpectedly highly soluble in 50% hydrogen peroxide. It solubilizes without an exotherm (temperature increase).

[0038] The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

(b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

[0039] The solution is mixed until a homogenous solution has been formed. The solution is allowed to mix by diffusion or by using a mixing device that is suitable for mixing liquids together. For example, 50% hydrogen peroxide can be introduced to a batch tank equipped with an overhead agitator blade. Triacetin can then be introduced to the 50% hydrogen peroxide when the agitator is in motion so that the components are thoroughly mixed.

[0040] The solution that is formed is a hydrogen peroxide-acetyl precursor solution, which also includes varying amounts of water, depending on the formulation used. When triacetin is used as the liquid acetyl precursor, the solution that is formed is a hydrogen peroxide-triacetin solution. One such hydrogen peroxide-triacetin solution comprises about 23% to about 40% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 20% to about 52% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor

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solution. The pH is about 1.46 to about 2.2 and no deliberate attempt is made to adjust the pH further.

[0041] A preferable hydrogen peroxide-triacetin solution comprises about 27.15% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 45.67% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor solution. The mole ratio of hydrogen peroxide:triacetin is about 3.8:1.

[0042] The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point of use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

Example 1

[0043] Triacetin (83.05 g) was added to 50% hydrogen peroxide solution (75 g) to form 158.05 g of a mixture. There was no evolution of gas indicating the hydrogen peroxide had decomposed to oxygen, nor was there any exotherm indicating that a chemical reaction had occurred. The solution did not turn oily or cloudy but remained clear. The solution was calculated to comprise 23.73% hydrogen peroxide and 52.55% triacetin, with the balance being water, and had a measured pH of 2.2. The mole ratio of hydrogen peroxide to triacetin was calculated to be 2.98:1. Titration of the solution immediately upon preparation yielded 24.1% hydrogen peroxide, which is within experimental error of the calculated amount of hydrogen peroxide.

[0044] This experiment showed that triacetin is remarkably soluble in 50% hydrogen peroxide. The solubility of triacetin was found to be at least 52.55%. This is surprising, given that the solubility of triacetin in water is only 7% at 25°C.

[0045] In order to test the stability of the mixture, the amount of hydrogen peroxide remaining and the amount of PAA generated was tracked for several months. The

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mixture was held at ambient temperature away from sources of light. Table I summarizes the data.

[0046] Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

Example 2

[0047] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 12.84:1 was prepared by adding triacetin (100.0 g) to 50% hydrogen peroxide (400.0 g) so that the mixture was 40% hydrogen peroxide and 20% triacetin, with the balance being water. The pH of the solution was 1.46 and the pH of a 1:100 dilution was 3.69. To accelerate storage characteristics, the sample was placed in an incubator set for 86-87°F. Table II shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of more than six months.

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[0048] Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

Example 3

[0049] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin (37.5008 g) to 50% hydrogen peroxide (65.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87°F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

Table III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

[0050] In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have

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been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

Example 4

[0051] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

Table IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

[0052] Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

Example 5

[0053] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 4.8:1 was prepared by adding triacetin (37.50 g) to 50% hydrogen peroxide (56.25 g) so that the mixture was 30% hydrogen peroxide and 40% triacetin, with the balance being water. The pH of the solution was 1.67 and the pH of a 1:100 dilution was 4.62. To accelerate degradation, the sample was placed in an incubator set for 86-87° F.

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Table V shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 43 days.

Table V

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	30.08	0.38
8	29.85	0.784
15	29.63	1.22
22	29.37	1.71
29	28.76	2.26
36	28.67	2.78
43	28.31	3.41

[0054] Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

Example 6

[0055] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.

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Table VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

~~[0056] Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.~~

~~Example 7~~

~~[0057] A 30-gallon batch of 50% hydrogen peroxide and triacetin was prepared by blending 137 lbs triacetin with 163 lbs 50% hydrogen peroxide so that the mixture was 27.15% hydrogen peroxide and 45.67% triacetin, with the balance being water. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The mixture was stored in an opaque drum in a non-climate controlled environment. On storage, the mixture slowly formed PAA in the container. Since this reaction of hydrogen peroxide to PAA does not represent a destructive loss of total peroxygen, to determine the true stability of the hydrogen peroxide, both the hydrogen peroxide and the peracetic acid generated must be quantified and reported as total peroxygen recovered.~~

~~[0058] After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate iodometric titration method, the PAA generated~~

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~~and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.~~

Table VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

~~[0059] After 295 days, 22.17% of the total peroxygen was recovered as either titratable hydrogen peroxide or hydrogen peroxide reacted to form PAA. To determine the stability of the peroxygen in the mixture, the total recovered hydrogen peroxide after 295 days (22.17%) was subtracted from the total recovered hydrogen peroxide of the initial theoretical value (27.17%). The result, 5%, is the loss of peroxygen (expressed as hydrogen peroxide) after 295 days of storage in a non-climate controlled environment.~~

43. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[~~0060~~0033] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[~~0061~~0034] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

(a) Providing water.

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[00620035] Flowing water is provided on a site having a point-of-use of peracetic acid.

[00630036] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[00640037] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[00650038] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[00660039] The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[00670040] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[00680041] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the

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water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[~~00690042~~] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[~~00700043~~] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For

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example, with 3/4" pipe, a static mixer of 3/4" diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0071<u>0044</u>] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. ~~A preferable~~<u>The</u> aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. ~~Other suitable alkali metal hydroxides include 45% potassium hydroxide.~~

[0072<u>0045</u>] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. ~~When~~ <u>With</u> the acetyl precursor ~~is~~ <u>as</u> triacetin, a ~~preferred~~ mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[0073<u>0046</u>] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0074<u>0047</u>] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[0075<u>0048</u>] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

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(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[00760049] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[00770050] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. ~~When~~ With the acetyl precursors ~~is as~~ triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[00780051] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the

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highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

[~~0079~~0052] In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

[0080] A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

(b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[~~0081~~0053] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[~~0082~~0054] ~~A preferable~~The liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[~~0083~~0055] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

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[00840056] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[00850057] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[00860058] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

(d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[00870059] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. ~~A preferable~~The aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. ~~Other suitable alkali metal hydroxides include 45% potassium hydroxide.~~

[00880060] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. ~~When~~ With the acetyl precursor ~~is~~ as triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

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[00890061] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[00900062] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[00910063] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[00920064] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. ~~When~~ With the acetyl precursors ~~is~~ as triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[00930065] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$$H_2O_2 = H^+ + HO_2^-$$

[00940066] The perhydroxyl anion (HO_2^-) then affects nucleophilic substitution

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reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. ~~When~~ With the acetyl precursor ~~is~~ as triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1,2,3-propanetriol (glycerine).

[~~0095~~0067] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. ~~When~~ With triacetin ~~is~~ used, assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is about 0.078% to about 1.88%.

[~~0096~~0068] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

[~~0097~~0069] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use, Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[~~0098~~0070] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

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[00990071] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

Example 81

[01000072] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for

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perhydrolysis.

Table VIII

Run #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remaining g	% Triacetin Converted to PAA
[illegible]	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
[illegible]	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
[illegible]	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
[illegible]	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
[illegible]	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
[illegible]	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
[illegible]	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
[illegible]	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
[illegible]	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
10	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
11	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
12	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
13	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
14	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
15	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
16	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
17	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
18	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
19	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
Dup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
20	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
Dup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
21	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
Dup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
22	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
23	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
24	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
25	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
26	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
27	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
28	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
29	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
30	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
32	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

[~~0101~~0073] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

~~Example 9~~

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[0102] A mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (63.4%) and triacetin (36.6%). Thus, the mole ratio of hydrogen peroxide:triacetin was 5.57:1. The mixture (13.68 g) was added to soft water such that the final solution contained 5 g/L of triacetin and had a pH of 4.1. Then, in successive experiments, sufficient 50% NaOH was added to the beaker so that the mole ratio of NaOH:TA was varied from 3:1 (obtained by introducing 5.49 g of 50% NaOH) to 8:1 (obtained by introducing 14.68 g of 50% NaOH). Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the 6:1 mole ratio of NaOH:TA are shown in Table IX.

Table IX

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
0	0.015	0.437	2.9
1	0.275	0.298	53.1
3	0.312	0.274	60.2
5	0.326	0.258	62.9
11	0.302	0.233	58.3
21	0.246	0.199	47.5

[0103] It can be seen that even before the introduction of 50% NaOH, some PAA was present in solution as a result of being generated in the diluted mixture of the two components. Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.326% occurring at five minutes, corresponding to a yield of 62.9% assuming all three acetyl groups of triacetin were available for perhydrolysis.

[0104] This exercise was repeated for mole ratios of NaOH: triacetin ranging from 3:1 to 8:1. Table X summarizes the next set of data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

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~~[0105] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.~~

Example ~~10~~2

[~~0106~~0074] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to about 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of about 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

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Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[~~0107~~0075] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[~~0108~~0076] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[~~0109~~0077] It can be seen that the amount of PAA generated, and hence the conversion of triacetin. into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

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Example ~~13~~

[~~01100~~0078] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 Acetyls)
1	0.247	0.208	47.3
3	0.280	0.178	53.6
5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[~~0111~~0079] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for per hydrolysis.

[~~0112~~0080] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the

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calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for per hydrolysis.

Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

[~~0113~~0081] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

~~Example 12~~

~~[0114] In the first test, a mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (54.24%) and triacetin (45.76%). Thus, the mole ratio of hydrogen peroxide:triacetin was 3.65:1. The mixture (51.22 g) was dissolved in soft water (911.9 g) in a one liter beaker to yield a solution with a pH of 6.47. Then, 50% NaOH (36.47 g) was introduced with stirring. Thus, the mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin was 4.2:3.8:1. The pH of the resulting solution initially measured 12.1. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes. It was noticed that the sample temperature rose immediately upon addition of the 50% NaOH.~~

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[0115] In the second test, the first test was repeated, except that the water was chilled soft water.

[0116] In the third test, the first test was repeated using three times the original amount of hydrogen peroxide:triacetin mixture and three times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (153.96 g) was introduced to chilled soft water (735.6 g) in a one-liter beaker to yield a solution with an initial pH of 5.14. Then, 50% NaOH (111.21 g) was introduced. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.

[0117] In the fourth test, the first test was repeated using four times the original amount of hydrogen peroxide:triacetin mixture and four times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (204.7 g) was introduced to chilled soft water (647.5 g) in a one-liter beaker to yield a solution with an initial pH of 6.32. Then, 50% NaOH (155.4 g) was introduced. Using the ceric sulfate iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.

[0118] Table XV summarizes the results obtained for the four tests and shows the initial and final solution temperatures, the pH of the solution after the addition of the 50% NaOH, the maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

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Table XV

Test #	Initial Temp. (°F)	Final Temp. (°F)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

[0119] Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

Table XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.6	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

[0120] The data in Tables XV and XVI indicate that far higher amounts of PAA are possible if the 50% sodium hydroxide solution is the last component of the mixture to be introduced. Further, up to 7.1% PAA was generated, although this solution got hot despite chilling the source water. Generation of the 6.3% PAA solution was very efficient because it represented a high 85.7% utilization of triacetin converted into PAA. There was clearly a linear relationship between Test 2, which generated 2.1% PAPA, and Test 3, which utilized three times more of the reactants and generated 6.3% PAA. The data in Table XV indicate that the time of maximum conversion of triacetin was between one and four minutes. Thereafter, the amount of PAA in solution is reduced because it undergoes high pH degradation slowly over the following 10 minutes.

Example 13

[0121] Fig. 1 is a schematic representation of an example of a system 10 that was used to perform an embodiment of one of the methods described above to prepare a non-equilibrium solution of PAA on a site having a point of use. Triacetin was used as the

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acetyl precursor and 50% sodium hydroxide was used as the aqueous source of an alkali metal hydroxide.

[0122] A container 120 of a hydrogen peroxide acetyl precursor solution, which was a hydrogen peroxide triacetin solution, and a container 140 of 50% sodium hydroxide were each equipped with chemical delivery diaphragm pumps 115 and 135, respectively. Inlet water 90, which was softened, was provided from a water source on the site having the point of use. Inlet water 90 was directed through a pressure regulator 100 and flow meter 105, then into a section of pipe where the hydrogen peroxide triacetin solution was introduced through injection quill 110. Mixing was accomplished using static mixer 125. Then, the sodium hydroxide solution was added through injection quill 130 to form a reaction medium.

[0123] The hydrogen peroxide triacetin solution and the sodium hydroxide solution may be added in a sequential manner as described, where the hydrogen peroxide triacetin solution was added first, or they may be added to the water simultaneously through a "T" fitting placed before static mixer 125. If a T fitting is used, the hydrogen peroxide triacetin solution and the 50% sodium hydroxide solution are introduced to opposite ends of the T fitting and the mixture is injected into the pipe of water. In other embodiments, the hydrogen peroxide and triacetin may be added separately, or sequentially, with either one first, or simultaneously, with the sodium hydroxide added either simultaneously with, or after, the hydrogen peroxide and triacetin.

[0124] The reaction medium was introduced to a residence chamber 145 which provided reaction time and contained a packing material to promote mixing. Residence chamber 145 was designed to be of a volume such that at a total flow rate of one gallon per minute, by the time the reaction medium reached sampling port 160, 30 seconds had elapsed since the sodium hydroxide solution had been added. A pH probe 155 monitored the pH of the mixture.

[0125] A controller 150 was interfaced to the flow meter 105 of the inlet water 90, and also to the chemical delivery diaphragm pumps 115 and 135. The controller 150 monitored the rate of the inlet water 90 and governed the rate at which the hydrogen

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peroxide triacetin solution and the NaOH solution were introduced. If the flow of inlet water 90 decreased because of lower PAA requirements at the point-of-use 195, the rates at which the hydrogen peroxide triacetin solution and the NaOH solution were pumped decreased accordingly. If the flow of inlet water 90 increased because of higher PAA requirements at the point of use 195, the rates at which the hydrogen peroxide triacetin solution and the NaOH solution were pumped increased accordingly. If the flow of inlet water 90 stopped, pumps 115 and 135 stopped. Thus, the generation of PAA was both continuous and intermittent, and was tailored to the PAA requirements at the point-of-use.

[0126] The rate of the reaction between the hydrogen peroxide and the triacetin to form PAA is dependent upon the temperature of inlet water 90. If the temperature of inlet water 90 is high (for example, about 70°F), the maximum conversion of triacetin into PAA may occur after 30 seconds, in which case the entire reaction medium was directed to the point of use 195. However, if the temperature of inlet water 90 is low (for example, about 32°F), longer reaction times may be necessary to maximize the conversion of triacetin into PAA. Then, the reaction medium was directed through one or more residence chambers 165, 175, and 185 which also contained a packing material to promote turbulence and cause thorough mixing. Residence chambers 165, 175, and 185 were designed to be of volumes such that at a total flow rate of one gallon per minute, the reaction medium reached sampling port 170 in one minute, sampling port 180 in two minutes, and sampling port 190 in five minutes, to permit sampling at different time intervals.

[0127] Thus, depending on the temperature of the inlet water, the time to achieve the maximum conversion of hydrogen peroxide and triacetin into PAA was determined by sampling and analyzing the solution at sample ports 160, 170, 180, and 190. The entire flow was then directed from the sampling port with the highest amount of PAA to the point of use 195. In practice, the PAA generated from the reaction of hydrogen peroxide with triacetin is typically diluted at the point of use 195.

[0128] Point of use 195 may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products;

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fruit and vegetable rinse water, or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

Example 14

[0129] Referring again to Fig. 1 , a 55-gallon drum container 120 of a hydrogen peroxide-triacetin solution was prepared by mixing triacetin (251.5 lbs) with 50% hydrogen peroxide (298.4 lbs). The resulting 550 lbs of hydrogen peroxide-triacetin solution had a specific gravity of 1.19 g/mL (10 lbs/gal) and contained 54.3% hydrogen peroxide and 45.7% triacetin. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The apparatus depicted in Fig. 1 was used to continuously and intermittently prepare an approximately 1% PAA solution.

[0130] Softened local city water was directed through pressure regulator 100 at a flow rate of one gallon per minute as measured by flow meter 105. The container 120 of hydrogen peroxide-triacetin solution was equipped with a draw down tube so that the flow rate of the mixture could be measured. Diaphragm pump 115 injected the hydrogen peroxide-triacetin solution through injection quill 110. The hydrogen peroxide-triacetin solution was then mixed with the softened water using static mixer 125. A container 140 of 50% NaOH was also equipped with a draw down tube to measure the flow pumped by diaphragm pump 135 into injection quill 130.

[0131] The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate-iodometric titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

Table XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide—Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37

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4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

[0132] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing flow rate of NaOH. For this mole ratio of hydrogen peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

Example 15

[0133] E. coliO157:H7 bacteria (ATCC 35150) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one liter test solutions.

[0134] Salmonella typhimurium bacteria (ATCC 14028) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one liter test solutions.

[0135] The amount of E. coliO157:H7 and Salmonella typhimuriumbacteria were measured by serial dilution and plating on 3ME, coliplates and 3MEnterobacteriaceaePetrifilms, respectively.

[0136] A 1000 ppm stock of PAA was made by weighing 0.6386 g of Perasan MP-2 (5.83% hydrogen peroxide and 15.66% PAA) and adding water up to 100 g. Perasan MP-2 is an equilibrium product of PAA (Enviro Tech Chemical Services, Inc., Modesto, California). Side by side, one of theE. coliand one of theSalmonellatest

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solutions were treated with a nominal dose of 1.0 ppm PAA by adding one mL of the 1000 ppm PAA stock solution to each sample. After one minute, approximately 100 mL of each test solution was removed, and sodium thiosulfate (0.5 g) was added to neutralize the PAA and hydrogen peroxide oxidants. After five minutes, sodium thiosulfate (0.5 g) was added to the remaining test solution to neutralize the PAA and hydrogen peroxide in the rest of the test solutions. The amount of viableE. coliO157:H7 andSalmonella typhimuriumbacteria remaining in the test solutions at the one minute and five minute contact times were measured by serial dilution and plating on 3ME. ColiPetrifilms and 3MEnterobacteriaceaePetrifilms, respectively.

[0137] A 1% solution of PAA was prepared by combining 30.90 g of a mixture of 50% hydrogen peroxide and triacetin (54.22% hydrogen peroxide and 45.78% triacetin) with 929.4 g of water, and then adding 50% NaOH (40.53 g). The PAA solution had a pH of 12.79. The mole ratio of this mixture was 3.8:7.8:1 NaOH:hydrogen peroxide:triacetin. One minute after preparation, the second one-liter E. Coli solution and the second one-liter Salmonella solution were treated with a nominal dose of 1.0 ppm PAA by adding 0.10 g of the 1% PAA solution to each sample. The test solution contact times, neutralization, and plating procedures were replicated for those that employed PAA from Perasan MP 2.

[0138] All 3ME. Coli Pertrifilms and 3MEnterobacteriaceaePetrifilms were incubated at 35°C for 24 hours. After incubation, the plates were enumerated.

[0139] Table XVIII shows the microbiological results of theE. coliO157:H7 test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. TheE. colitest solution started with log106.99 CFU/mL prior to being treated with 1.0 ppm of PAA from Perasan MP-2 or with 1 ppm of PAA from the 1% PAA solution.

[0140] TheE. colitest solution treated with 1.0 ppm PAA from Perasan MP 2 contained a log106.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log106.34 CFU/mL remained (77.50% reduction). The E. coli solution treated with a nominal 1.0 ppm PAA from the 1% PAA solution

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contained a log106.78 CFU/mL after one minute and 6.63 CFU/mL after five minutes, respectively, corresponding to 38.02% and 56.12% reductions, respectively.

Table XVIII

E. coli O157:H7			
Description	log_{10} CFU/ml remaining	log_{10} reduction	% reduction
Control	6.99	N/A	N/A
Perasan MP-2 (1 min)	6.74	0.25	43.48
Perasan MP-2 (5 min)	6.34	0.65	77.50
1% PAA solution (1 min)	6.78	0.21	38.02
1% PAA solution (5 min)	6.63	0.36	56.12

[0141] Table XIX shows the microbiological results of the Salmonella typhimurium test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. The Salmonella test solution started with log107.07 CFU/mL prior to being treated with PAA from Perasan MP 2 or with the 1% PAA solution.

[0142] The Salmonella solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log101.76 CFU/mL after one minute and 0.70 CFU/mL after five minutes, corresponding to >99.999% reduction at both contact times. The Salmonella test solution treated with 1.0 ppm PAA from the 1% PAA solution contained a log106.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log104.95 CFU/mL remained (99.24% reduction).

Table XIX

Salmonella typhimurium			
Description	log_{10} CFU/ml remaining	log_{10} reduction	% reduction
Control	7.07	N/A	N/A
Perasan MP-2 (1 min)	1.76	5.31	99.9995
Perasan MP-2 (5 min)	0.70	6.37	>99.9999
1% PAA solution (1 min)	6.69	0.38	58.31
1% PAA solution (5 min)	4.95	2.12	99.24

[0143] The data in tables XVIII and XIX demonstrate that the 1 % PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%,

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about equal to that of the Perasan MP-2, which was > 99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

[0144] A freely flowable, solid peroxygen bleaching and stain removal composition comprises a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. A preferable liquid acetyl precursor is triacetin. The water-soluble solid source of hydrogen peroxide is preferably sodium percarbonate, although sodium perborate monohydrate or sodium perborate tetrahydrate may be used. The water-soluble solid source of alkalinity acts as a pH control agent, and may be an alkali metal or earth alkali metal bicarbonate, carbonate, sesquicarbonate, borate, silicate, or hydroxide. Examples include sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, sodium borate, sodium borate decahydrate (borax), sodium metasilicate, and sodium hydroxide.

[0145] In an embodiment, the composition comprises about 0.99% to about 8.45% triacetin, about 13% to about 54% sodium percarbonate, and about 24% to about 44% solid source of alkalinity.

[0146] The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispercency, and lower surface tension.

[0147] Metal ions present in the bleaching medium can have a tendency to deposit on the substrates being bleached. Therefore, the solid bleaching composition may optionally contain a metal chelating agent such as a polyacrylate, a phosphonate, a maleic acid, a salt of ethylenediaminetetraacetic acid, a salt of nitrilotriacetic acid, or a salt of gluconic acid.

[0148] Surfactants reduce the surface tension of the bleaching medium and enhance the process of cleaning the soiled article. Surfactants also disperse the soil particles removed from the article and keep them suspended. Therefore, the solid bleaching

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composition may optionally contain a surfactant, such as an anionic, cationic, amphoteric, or non ionic surfactant.

[0149] The solid bleaching composition may also optionally contain a solid zeolite, such as sodium zeolite, which acts to capture calcium and magnesium ions that may be present in the bleaching medium that would otherwise interact with an anionic surfactant, causing the surfactant to precipitate and removing it from the bleaching medium.

[0150] The composition may also optionally contain an inert, solid filler, such as anhydrous sodium sulfate, sodium sulfate decahydrate, or sodium chloride. The filler increases the total ionic strength of the aqueous phase, but imparts no chemical properties to the bleaching medium.

[0151] To make the solid peroxygen bleaching and stain removal composition, the water soluble solid source of hydrogen peroxide, the water soluble solid source of alkalinity, any chelating agent, any sufactant, and any filler are blended with the liquid triacetin to form a solid bleaching composition. The components may be added in any order. Any blending equipment may be used. Suitable examples of equipment include a ribbon and paddle blender, a V and double cone blender, a Nauta screw mixer, and a rotating cement mixer. Alternatively, the ingredients may be blended by milling using a pulveriser mill, a ball mill, a hammer mill, a pin mill, an air mill, or a roller mill. Blending is performed for sufficient time to create a homongenous mixture. The mixture is a freely flowable solid which is readily discharged from the blender.

Example 16

[0152] A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.

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Table XX

Component	%
Sodium carbonate, anhydrous	26.3
Sodium percarbonate	58.9
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

[0153] This solid peroxygen bleach precursor was then blended with incrementally increasing amounts of liquid triacetin. At each addition, the product was examined for flowability and for the odor of PAA. Table XXI summarizes the findings when up to 9.1g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

Table XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely- flowable solid	None
2	Freely- flowable solid	None
3	Freely- flowable solid	None
4	Freely- flowable solid	None
5	Freely- flowable solid	None
6	Freely- flowable solid	None
7	Freely- flowable solid	None

(continued)

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
8	Freely- flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

[0154] Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45g of the triacetin to form a freely-flowable solid composition, without becoming a sticky, non-flowable product which would not pour easily or would become a solid mass upon storage inside a container.

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[0155] The solid peroxygen bleaching and stain-removal composition was calculated to contain the following percentage of components, listed in Table XXII.

Table XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

[0156] Another unexpected result was that after storing the composition for over one year at ambient temperature, the composition still had not developed an odor of PAA.

[0157] These surprising results are in contrast to the current belief that a liquid acetyl precursor, such as triacetin, could not be utilized with a solid source of hydrogen peroxide in a non-chlorine peroxygen bleaching and stain removal composition, for at least two reasons. First, when a non-chlorine peroxygen bleaching composition is used in residential and commercial laundering applications, the product must be a freely flowable solid. Typically, the acetyl precursor in a non-chlorinated peroxygen bleach is present in amounts up to 10%. It was believed that blending a liquid at this level with the other dry components of the laundry bleach would create a sticky, clumping mass, rather than a freely flowable solid, and would therefore not be acceptable to the user. Second, it was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

Example 17

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~~[0158] Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.~~

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Table XXIII

Components of Composition A	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	41	615

(continued)

Components of Composition A	%	Charge Weights, g
Premix 1		
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	4	60
Soda Ash	16	240

Components of Composition B	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	43	645
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	2	30
Soda Ash	16	240

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[0159] In both cases, Premix 1 was prepared by kneading the NANSA HS 90 (a sodium dodecylbenzenesulfonate surfactant) with the sodium sulfate. The sodium sulfate helped break up the sticky surfactant efficiently. Then, the sodium percarbonate, the sodium metasilicate, and the triacetin were added and mixed by hand.

[0160] In both cases, Premix 2 was prepared by mixing the sodium hydroxide beads with the mineral oil to afford a well coated mixture, with some free standing mineral oil remaining. Soda ash was blended in portions to take up the excess liquid and to provide a free flowing solid mixture.

[0161] Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

[0162] Both compositions A and B, which were held in uncovered bowls at ambient temperature after preparation, exhibited slow weight gain over time, most likely due to absorbance of water from the air. Each composition had gained 2.4% of its initial weight over a period of three days.

[0163] Neither composition exhibited significant exothermic behavior. However, composition A was hotter at the end of preparation and cooled more slowly than composition B. The temperature of composition A was 85°F immediately after preparation, rose to 88°F over the next ten minutes, and then fell slowly to 74°F. The temperature of composition B was 80°F immediately after preparation, rose to 81°F over the next twenty minutes, and then fell slowly to 65 °F.

[0164] The solid peroxygen bleaching and stain removal composition described above may be used as follows.

[0165] First, the solid peroxygen, composition is introduced to an aqueous medium that is used for bleaching or stain removal of at least one article contained within the aqueous medium. For bleaching of laundry articles, about 5g of bleaching composition is introduced for every liter of water used in the bleaching cycle. For home use, the bleaching composition can be added manually at the start of the wash.

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For commercial laundry systems, the bleaching composition may be introduced just before the bleaching cycle, toward the end of the wash and following the soil removal cycle. In most commercial and residential laundry machines, bleaching cycles are typically about 10-15 minutes.

[0166] Second, the composition is allowed to dissolve and react to form the bleaching medium containing PAA. The solid source of hydrogen peroxide, such as sodium percarbonate, and the solid source of alkalinity, such as sodium hydroxide, dissolve in the laundry water and cause the pH of the water to increase to above about 10.5.

[0167] While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

[0168] The perhydroxyl anion (HO_2^-) then effects nucleophilic substitution reactions on the carbonyl groups of triacetin, in a perhydrolysis reaction, to form PAA and 1,2,3 propanetriol (glycerine). The laundry water would also contain unreacted hydrogen peroxide, unreacted triacetin, and sodium hydroxide.

[0169] Third, the aqueous solution of PAA and the unreacted hydrogen peroxide are mixed for sufficient time to effect bleaching or stain removal of the articles contained within the aqueous medium. Both commercial and residential bleaching cycles are about 10-15 minutes.

[0170] Fourth, the article is rinsed with fresh water so that it becomes substantially free of PAA and the unreacted hydrogen peroxide, the glycerine, the unreacted triacetin, and the sodium hydroxide. Generally, for a laundered article, the washing machine is programmed to empty the bleaching medium and replace it with fresh water. The machine can agitate the articles with the rinse water to enhance the rinsing process.

[0171] Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically

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dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

Example 18

[0172] Laundry swatches were made by cutting a tea towel into 50 equal 5 x 4 inch sheets. They were then separated into seven groups of seven swatches. Six of the groups were stained and the seventh group was left unstained for comparison purposes. Five of the groups that were stained were stained by soaking them in one of the following: black tea, black coffee, red wine, blood (pork), and acetone extracted chlorophyll. The sixth group of swatches was stained by rubbing them on green grass. After allowing the stained swatches to dry, and before challenging the stains, the swatches were set aside for two months to allow the stains to set in the fabric.

[0173] A solid peroxygen bleaching and stain removal composition (200 g) was prepared by blending sodium percarbonate (104.0 g), triacetin (8.00 g), soda ash (80.01 g), and sodium hydroxide beads (8.00 g). The final product was a freely flowable solid.

[0174] The composition was tested using 1:100 dilution at both 75°F and 104°F. The initial pH was measured and the concentrations of PAA and hydrogen peroxide were evaluated using the method of U.S. patent no. 7,651,724 . At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75°F, the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104°F had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H2O2). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75°F at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104°F at a pH of 11.2.

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Table XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

Table XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426

(continued)

Time (min)	ppm PAA	ppm Hydrogen Peroxide
5.5	133	1494
7.8	122	1427
10.3	119	1405

[0175] The stain removal ability of the composition was determined by comparing treated swatches to control swatches (swatches washed in just city water for the same amount of time and at elevated temperature) and non-stained swatches. The description of the swatches is set forth in Table XXVI. Three stained swatches were used for each test. The composition (10.0 g) was weighed into a beaker (2000 mL). To this beaker a measured amount of hard water (990.0 g) was added at ambient

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temperature (64°F). The swatches were added to the solution and agitated by mixing with a plastic utensil for 10 minutes to simulate a laundry bleaching cycle. After 10 minutes, the wash water was discarded and a water rinse was performed by adding fresh city water (1000.0 g) to the swatches and agitating for two minutes using the same plastic utensil. The swatches were immediately removed from the beaker after rinsing, wrung out by hand, and laid to dry. These steps were then repeated using water at an elevated temperature (120°F).

[0176] A control swatch was obtained by taking one swatch at a time from each stain group and washing in city water at an elevated temperature (120°F) for 10 minutes in the same manner as the treated swatches. After the wash, the swatches were immediately removed, wrung out by hand, and laid to dry.

Table XXVI

Type of Swatches	Description
Treated Swatches	Swatches subjected to bleaching for 10 minutes using bleaching formulation with triacetin and a 2 minute rinse with hard water
Control Swatches	Swatches subjected to only an elevated temperature (120°F) hard water wash for 10 minutes
Non-Stained Swatches	Non-altered swatches

[0177] The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

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Table XXVII

Type of Stain	Bleaching Formula at 64°F	Bleaching Formula at 120°F
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

~~[0178] It can be seen that, in general, the composition displayed enhanced stain removal properties at elevated temperature. Excellent stain removal properties were obtained for black tea and black coffee, and more moderate performance with red wine and blood. The composition had virtually no effect on grass stains or the chlorophyll pigment that was acetone extracted from green grass.~~

~~[0179] The invention has been described above with the reference to the preferred embodiments. Those skilled in the art may envision other embodiments and variations of the invention that fall within the scope of the claims.~~

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BY FACSIMILE

Our ref.: AT-X11031DIV2-EP
Your ref.: 8658/17669P
02 Sept 2015

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Further to issuance of the communication under Rule 70(2) and 70a(2) EPC dated 9th March 2015 and the extended European Search Report, please find enclosed amended pages of the application, together with a marked up version of the pages as amended and an indication below as to the amendments that have been made.

Claim Amendments

Claim 1 has been amended to include the subject matter of previous claims 6 and 7 of the application.

Previous claims 2-8 of the application have been deleted.

Previous claim 9 (now claim 2) has been amended to remove the wording "sufficient time" and to introduce the time period of previous claim 10.

Previous claims 10, 11, 13-14 of the application have been deleted.

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Previous claim 12 (now claim 3) has been amended to remove the word "about".

Objections in the Search Report

With regard to point 1 of the Search Report, claim 1 of the granted parent patent requires the feature of introducing a hydrogen peroxide-triacetin solution to water and the mole ratio of the three compounds. Newly amended claim 1 of the present application requires introducing the triacetin and hydrogen peroxide to water, as two separate components and not a single mixture of triacetin and hydrogen peroxide. Newly amended claim 1 does not include the mole ratio of the three compounds.

With regard to point 2 of the Search Report, the words "about" and "sufficient time" have been deleted from the claims. The system units for the sodium hydroxide have been included in amended claim 1. Previous claims 9 and 10 have been combined to form newly amended claim 2 which is no longer defined in terms of a result to be achieved. Previous claims 11, 13-14 have been deleted.

With regard to points 3 and 4 of the Search Report, claim 1 of the application has been amended to include the subject matter of previous claims 6 and 7. The examiner has already indicated that the subject matter of previous claim 7 is novel and inventive over the cited prior art.

With regard to point 5 of the Search Report, reference to D1-D4 has been made on page 7 of the present application. Reference to D5 is already provided on pages 5-6 of the application.

The description of the application has been brought into conformity with the amended claims.

We trust the above amendments are now sufficient to place the application in order for grant and we look forward to receiving confirmation to this effect in due course. In the event the examiner intends to reject the present application without providing the applicant with one or more opportunities for responding to the objections in writing, we hereby request Oral Proceedings under Art. 116 EPC in respect of this matter.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

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2. Sep. 2015 15:04 bailey walsh & co No. 5876 P. 2

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Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 301

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Bailey Walsh & Co LLP
1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date
09.03.15

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Communication pursuant to Rules 70(2) and 70a(2) EPC and reference to Rule 39(1) EPC

The date on which the European Patent Bulletin mentions the publication of the European search report for the above-identified European patent application (publication number: 2842423) is 04.03.15.

Since the request for examination has been filed (R. 70(1), Art. 94(1) EPC) prior to the transmission of the European search report, you are hereby invited to indicate whether you desire to proceed further with the application.

If you do not reply to this invitation within **six months** of the above-mentioned publication date, the application **will be deemed to be withdrawn** (R. 70(3) EPC).

You are invited, within the above-mentioned six-month period, to comment on the objections raised in the opinion accompanying the European search report and/or to file any amendments to the description, claims and drawings correcting any deficiencies noted in the opinion (R. 70a(2), R. 137(2) EPC; Guidelines for Examination in the EPO, B-XI, 8).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

Should the reply to the invitation pursuant to Rule 70a(2) EPC be filed in an admissible non-EPO language, a translation is to be submitted within one month of its filing (R. 6(2) EPC).

Should you not comply with this invitation within the time limit, the application **will be deemed to be withdrawn** in accordance with Rule 70a(3) EPC.

Note
If not yet paid, the designation fee is also payable within **six months** of the above-mentioned publication date (R. 39(1) EPC).
This period for payment is applicable for extension and validation fees as well.

The present amount of the designation fee is EUR 580,00.

Note to users of the automatic debiting procedure
Unless the EPO receives prior instructions to the contrary, the designation fee will be debited on the last day of the period for payment. For further details see the Arrangements for the automatic debiting procedure, Supplementary publication 4 - OJ EPO 2014.

Registered letter
EPO Form 1082 04.14 (NFS/RTB/ESOP01=N)

Important information concerning fee amounts
Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment.** The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website (**www.epo.org**) and can be found under **www.epo.org/schedule-of-fees**, which allows the viewing, downloading and searching for individual fee amounts, both current and previous.
Please note that procedural fees are usually adjusted every two years, on even years, with effect from 1 April.

Payments by cheque delivered or sent direct to the EPO are no longer accepted as from 1 April 2008 (see OJ EPO 2007, 626).

Note concerning renewal fees
Under Article 86 EPC renewal fees shall be paid to the EPO for the European patent application. These fees shall be due in respect of the third and each subsequent year, calculated from the date of filing. Due account should be taken that the EPO will not send invoices or reminders to pay any fees in due time.

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Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 303

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Tomkinson, Alexandra
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1 York Place
Leeds, LS1 2DR
ROYAUME UNI

Date: 04.03.15

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454 / 2842423

Applicant/Proprietor: Enviro Tech Chemical Services Inc.

Refund of fees

The following fee(s) was (were) paid in respect of the application 14185786.2:

Fee	Reference	Voucher No	Date	Currency	Amount
Search fee	002	01096854	22.09.14	EUR	1 285,00

The fee(s) was (were) paid by Bailey Walsh & Co..

According to the present state of the file the refund will be made by:

CREDITING THE DEPOSIT ACCOUNT 28050202 Bailey Walsh & Co..

Amount refundable:	Reference	Currency	Amount	Voucher No
	002	EUR	1.285,00	00631942

Reason for refund: Full use of earlier European search report with written opinion drawn up by the EPO (100 % of fee paid for current search refunded).

The Authorising Officer
Aitken
(49)(89)23992735

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EPO Form 2907 04.14

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Date
04.02.15

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454 / 2842423
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Notification of European publication number and information on the application of Article 67(3) EPC

You are hereby informed that the technical preparations for the publication of the above-mentioned European patent application have been completed.

The application will be published on 04.03.15 with the European search report.
The publication number is: 2842423.
The publication will be mentioned in European Patent Bulletin number 2015/10.
(**http://bulletin.european-patent-office.org**).

The provisional protection under Article 67(1) and (2) EPC in the individual contracting states becomes effective only when the conditions referred to in Article 67(3) EPC have been fulfilled. For further information, also with respect to extension states, please refer to the EPO brochure "National Law relating to the EPC" (**http://www.epo.org/patents/law/legal-texts/national-law-epc.html**).

The title of the invention in the three official languages of the European Patent Office is worded as follows:

> Verfahren und Zusammensetzungen zur Erzeugung von Peressigsäure direkt am Verwendungsort
> Methods and compositions for the generation of peracetic acid on site at the point-of-use.
> Procédés et compositions pour la génération d'acide peracétique sur site au niveau du point d'utilisation

In all future communications to the EPO, please quote the application number as indicated above, i.e. including the final four figures (which identify the Directorate responsible for the subsequent procedure).

Remark
The publication can be downloaded, free of charge, from the EPO publication server **https://data.epo.org/publication-server/** or can be ordered from the Vienna sub-office upon payment of a fee (see Decision of the President of the EPO dated 12 July 2007 concerning the form of publication of European patent applications, European search reports and European patent specifications, Special edition No. 3, OJ EPO 2007, 97).

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Applicants wishing to accelerate proceedings before the EPO may file a request according to the programme for accelerated prosecution of European patent applications - "PACE" (OJ EPO 2010, 352). EPO Form 1005 is available on the EPO website (www.epo.org) for this purpose.

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Petitioner's Exhibit 1022
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Date
30.01.15

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Communication

The extended European search report is enclosed.

The extended European search report includes, pursuant to Rule 62 EPC, the European search report (R. 61 EPC) or the partial European search report/ declaration of no search (R. 63 EPC) and the European search opinion.

Copies of documents cited in the European search report are attached.

☑ 0 additional set(s) of copies of such documents is (are) enclosed as well.

The following have been approved:

☐ Abstract ☑ Title

☑ The Abstract was modified and the definitive text is attached to this communication.

The following figure(s) will be published together with the abstract: 1

Refund of search fee
If applicable under Article 9 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.

Should you wish to further prosecute this application in the examination phase, your attention is drawn to the provisions of Rule 70a EPC. An invitation to respond to the extended European search report will be issued once the date of publication of the European search report has been mentioned in the European Patent Bulletin (R. 69(1), R. 70(2) EPC).

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The examination is being carried out on the **following application documents**

Description, Pages

1-59	filed on	24-03-2011

Claims, Numbers

1-14	filed on	24-03-2011

Drawings, Sheets

1	filed on	24-03-2011

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 EP 1 618 786 A1 (KAO CORP [JP]) 25 January 2006 (2006-01-25)

D2 JP 2004 230323 A (MATSUSHITA ELECTRIC IND CO LTD) 19 August 2004 (2004-08-19)

D3 US 2010/227000 A1 (AMES KELLY ANN [GB] ET AL BOARD KELLY ANN [GB] ET AL) 9 September 2010 (2010-09-09)

D4 US 6 221 341 B1 (MONTGOMERY R ERIC [US]) 24 April 2001 (2001-04-24)

D5 WO 01/46519 A1 (WARWICK INTERNAT GROUP LTD [GB]; WITHENSHAW JOHN DAVID [GB]; SKETT MAT) 28 June 2001 (2001-06-28)

The present application concerns a method for generating a non-equilibrium solution of peracetic acid in water. A solution of hydrogen peroxide and triacetin is added to water and a solution of a metal hydroxide is added to the mixture and stirred. The method is used in mixing tanks or under aqueous stream.

1 Article 76(1) EPC

1.1 The requirements of article 76(1) are met:

1.2 The subject-matter does not extend beyond the content of the earlier application, as filed.

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1.3 The attention of the applicant is drawn to the fact that the parent and the divisional application may not claim the same subject-matter, in order to avoid double patenting (see GL 2012, C-IX, par. 1.6). Independent claim 1 appears to be identical to independent claim 1 of the parent application. Also dependent claims 4 to 14 are identical to some of the dependent claims of the parent application.

1.4 It is an accepted principle that two patents cannot be granted to the same applicant for one invention (se G 1/05, and G 1/06). It is permitted to allow an applicant to proceed with two applications having the same descriptions where the claims are quite distinct in scope and directed to different inventions.

1.5 The applicant must either amend the parent or the divisional applications in such a manner that the subject-matter of the claims of the applications is not identical, or choose which one he wishes to proceed to grant. If the applicant is not doing so, once one of the applications is granted, the others will be refused under Art. 97(2) in conjuction with article 125 (see GL 2012, C-IV, par. 5.4).

2 Clarity (Article 84 EPC)

2.1 The application does not meet the requirements of Article 84 EPC, because claims 7, 9-12, 13-14 are not clear.

2.2 Claims 7 and 10 to 12 are considered as unclear because of the use of the term "about". The terms "about" used in claims 7 and 10 to 12 are vague and unclear and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claims unclear (Article 84 EPC).

2.3 Claims 7 is not clear because the amount of sodium hydroxide is not expressed precisely, since the system units are missing. System units are explained on p.13, par. [0031] of the description, nevertheless the meaning of the claim should be clear from its wording as such, without the need of explanations made in the descriptions.

2.4 Claim 9 is considered as unclear because of the use of a vague term, that is "sufficient time". This term has a relative meaning and renders the claim unclear. Claim 10 attempts to clarify the claim on which it depends, by giving the exact time interval that is required and that would render the meaning of claim 9 clear.

2.5 Claim 9 and claim 11 do not meet the requirements of Article 84 EPC in that the matter for which protection is sought is not defined. The claims attempt to define the subject-matter in terms of the result to be achieved. Such a definition is only allowable under the conditions elaborated in the Guidelines F-IV, 4.10. In this instance, however, such a formulation is not allowable because it appears possible to define the subject-matter in more concrete terms, viz. in terms of how the effect is to be achieved. This has been done by defining mole ratios between the components. This

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could be done by defining the time-interval after which a subsequent "cycle" can be started. The amount of converted triacetin is a result of the mole ratio of the components and a result of the time interval.

3 Novelty (Article 54(1) and 54(2) EPC)

3.1 The present application does not meet the requirements of Article 52(1) EPC because the subject-matter of claims 1, 2, 5-6, 8, 14 is not new within the meaning of Article 54(1) and (2) EPC.

3.2 **D1** describes a process for the production of a bactericide based on an organic peracid. The sterilizing agent is a water based solution obtained by combining triacetin and hydrogen peroxide. The ratio between these two component has to be comprised between 1/10 and 20/1. The variation in the peroxyacid concentration is controlled (par. [0082-[0084], example 1, tables 1 to 5). Table 10, example 3 displays the control of *Bacillus cereus* and *B. subtilis* by triacetin solutions comprising hydrogen peroxide to which a base is added to regulate the pH. Table 11 displays a formulation which comprises 50% by weight of triacetin, 15% of hydrogen peroxide, 0.17% of hydrogen peroxide and 57.3% of remaining peroxide. **D1** is considered as novelty destroying for claims 1, 2, 5-6, 8, 14.

3.3 **D2** is considered as novelty destroying for claims 1, 2, 5-6. It describes a sterilising agent for hard surfaces. Triacetin is used as the agent capable of liberating acetic acid, hydrogen peroxide is to be added and a metal hydroxide has to be used to bring the pH to 8-12. Paragraph [0057] describes an example where 0.23 mol of triacetin, 0,73 of hydrogen peroxide and 0,5 of sodium hydroxide are used.

3.4 **D3** describes a solid constituent A that is an acetyl source (TAED preferably) and that is combined with a liquid part B that is an aqueous solution of hydrogen peroxide (5-10% by wt.). A water solution of 0.05 to 5% alkali is also added by adding sodium hydroxide. The pH is maintained between 5 and 8 and the PAA generation takes 5 to 15 minutes. It is a method to generate PAA using a kit of parts where one part is the solid acetyl donor and another part is the liquid composition of hydrogen peroxide.

3.5 **D4** discloses a teeth whitening composition. Peracetic acid is the whitening agent and is generated by glyceryl triacetate with the addition of hydrogen peroxide and in the presence of a base that regulates the pH. The most favourable conditions are at higher pH where the whitening agent works faster. The human use determines the reagent and the conditions used (col. 3, l. 55-col. 4, l. 57, col. 5, l. 58-col. 7, l. 16 and col. 7, l. 60-col. 8, l. 23, examples I-III and V).

4 Inventive Step (Article 56 EPC)

4.1 Claims 3, 4 and 13

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4.1.1 The present application does not meet the requirements of Article 52(1) EPC because the subject-matter of claims 3, 4 and 13 does not involve an inventive step within the meaning of Article 56 EPC.

4.1.2 **D1** is considered to be the prior art closest to the subject-matter of claims 4 and 13 discloses the production of a bactericide based on peracetic acid.

4.1.3 The subject-matter of claim 4 and 13 therefore differs from this known **D1** in that the bactericide is prepared in an aqueous stream and not in a tank.

4.1.4 According to the present application, the point of use can be at the end of a pipe where water is injected and subsequently the required components (triacetin-hydrogen peroxide solution and hydroxide solution respectively) are added simultaneously or one after the other.

4.1.5 The problem to be solved by the present invention may therefore be regarded as how to provide a method that generates a non-equilibrium solution of peracetic acid in an aqueous stream.

4.1.6 The solution proposed in claims 4 and 13 of the present application cannot be considered to involve an inventive step (Articles 52(1) and 56 EPC). Continuous peroxiacid generating systems are known in the art as in the case of **D5**, where a different source of acetyl groups is used rather than triacetin. **D5** discloses a pipe system (see Fig. 1) where hydrogen peroxide and TAED are introduced in a mixer and subsequently hydroxide anions are added as a solution of sodium hydroxide (p. 3, l. 6-10, p. 4, l. 14-28). A final container allows further mixing with the last added ingredient (p. 8, l. 14-26). The person skilled in the art would not need to use any inventive skill to adapt the steps of the present application to a pipe system like the one of **D5**. An inventive step can not be acknowledged for claims 4 and 13.

4.1.7 It is evident that adding the two ingredients one after the other rather than simultaneously cannot be considered as inventive, in particular, if no effect is related with the addition in a certain order. Claim 3 is therefore also considered as non-inventive.

4.2 Claims 7 and 12

4.2.1 The subject-matter of claim 12 therefore differs from this known **D1** in that the ratio between the components does not correspond to the ratio disclosed in claim 12. A higher amount of metal hydroxide is used in the present application.

4.2.2 According to the present application, when the hydroxide solution is added and the pH is highly alkaline, the reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA.

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4.2.3 The problem to be solved by the present invention may therefore be regarded as how to provide an alternative method of preparation of a solution of peracetic acid (PAA) that is not at the equilibrium.

4.2.4 The solution proposed in claim 12 of the present application can be considered to involve an inventive step (Articles 52(1) and 56 EPC). The displayed examples show the rapid generation of PAA and a sanitizing effect on *E. coli* and *Salmonella* strains. The man skilled in the art, although aware of the possibility of using the same ingredients (triacetin, hydrogen peroxide and sodium hydroxide), would not have been able, starting from **D1** to solve the problem posed in the same way without needing an inventive step. The solution proposed in claim 12 is therefore considered to involve an inventive step.

4.2.5 The same conclusions would be valid for claim 7 that refers to the amount of sodium hydroxide. Nevertheless, the claim is considered as not clear because of the absence of the units expressing the percent. Claim 7 is considered as non obvious, if the amount to which it is referred are weight percent as indicated on p. 13, par. [0031] of the description. Nevertheless, the inventive step cannot be acknowledged for a claim that is not worded in a clear way.

4.3 Claims 9 to 11

4.3.1 Notwithstanding the above-mentioned lack of clarity, the subject-matter of claims 9 to 11 is considered to be non obvious.

4.3.2 It appears that a 1% PAA solution, after a certain amount of time can be as efficient as commercial solutions of much higher concentration of peracetic acid. It seems not obvious that a waiting time could help in the achievement of a higher antibacterial effect.

4.3.3 Nonetheless, a clear wording of claim 9 is necessary in order for the inventive step to be acknowledged.

5 Acknowledgement of the Prior-Art

5.1 To meet the requirements of Rule 42(1)(b) EPC, **D1** to **D5** should be identified in the description and the relevant background art disclosed therein should be briefly discussed.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 18 5786

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	EP 1 618 786 A1 (KAO CORP [JP]) 25 January 2006 (2006-01-25) * paragraphs [0001] - [0005], [0023] - [0025], [0046] - [0047] * * example 1; tables 1-5 * * example 3; table 10 * * example 4; table 11 * * example 6; tables 23, 24 * -----	1-3,5,6, 8,14 4,13	INV. A01N37/16 A01N25/00 A61K31/075 A61L9/00 A61L2/18 A61K31/327
X	JP 2004 230323 A (MATSUSHITA ELECTRIC IND CO LTD) 19 August 2004 (2004-08-19) * abstract * * paragraphs [0001], [0008], [0011] - [0014], [0057] * -----	1,2,5,6	
A	US 2010/227000 A1 (AMES KELLY ANN [GB] ET AL BOARD KELLY ANN [GB] ET AL) 9 September 2010 (2010-09-09) * paragraphs [0002] - [0006], [0012], [0016] - [0017], [0051] - [0061], [0064], [0083] - [0097] * -----	1-14	
			TECHNICAL FIELDS SEARCHED (IPC)
A	US 6 221 341 B1 (MONTGOMERY R ERIC [US]) 24 April 2001 (2001-04-24) * column 3, line 55 - column 4, line 57 * * column 5, line 58 - column 7, line 16 * * column 7, line 60 - column 8, line 23 * * examples I-III, V * -----	1-14	A01N
Y	WO 01/46519 A1 (WARWICK INTERNAT GROUP LTD [GB]; WITHENSHAW JOHN DAVID [GB]; SKETT MAT) 28 June 2001 (2001-06-28) * page 1, line 1 - line 23 * * page 2, line 3 - line 12 * * page 3, line 6 - line 10 * * page 4, line 14 - line 28 * * page 6, line 9 - line 24 * * page 8, line 14 - line 26 * * figure 1 * -----	4,13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 January 2015	Zanobini, Alessandra

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 14 18 5786

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-01-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1618786 A1	25-01-2006	EP 1618786 A1	25-01-2006
		KR 20050114707 A	06-12-2005
		TW I379641 B	21-12-2012
		US 2007274857 A1	29-11-2007
		WO 2004089089 A1	21-10-2004
JP 2004230323 A	19-08-2004	NONE	
US 2010227000 A1	09-09-2010	CA 2754495 A1	10-09-2010
		CN 102413846 A	11-04-2012
		EP 2403541 A1	11-01-2012
		JP 5576408 B2	20-08-2014
		JP 2012519702 A	30-08-2012
		RU 2011140353 A	10-04-2013
		US 2010227000 A1	09-09-2010
		WO 2010102188 A1	10-09-2010
US 6221341 B1	24-04-2001	US 6221341 B1	24-04-2001
		US 2001021374 A1	13-09-2001
		US 2004101497 A1	27-05-2004
WO 0146519 A1	28-06-2001	AU 5441701 A	03-07-2001
		WO 0146519 A1	28-06-2001

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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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Date
28.01.15

Reference	Application No./Patent No.
	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Designation as inventor - communication under Rule 19(3) EPC

You have been designated as inventor in the above-mentioned European patent application. Below you will find the data contained in the designation of inventor and further data mentioned in Rule 143(1) EPC:

DATE OF FILING : 24.03.11

PRIORITY : / /

TITLE : Methods and compositions for the generation of peracetic acid on site at the point-of-use.

DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

INVENTOR (PUBLISHED = 1, NOT PUBLISHED = 0):

1/Harvey, Michael .S./712, Faust Road/Modesto, CA California CA95358/US
1/Howarth, Jonathan . N./3804 Vader Drive/Modesto, CA 95356/US

DECLARATION UNDER ARTICLE 81 EPC:
The applicant(s) has (have) acquired the right to the European patent as employer(s).

Receiving Section

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Associates: P. Stephenson, MSci, PhD, MRSC, CPA, EPA
M. Kellett, MITMA
D. Corbyn, MChem, EPA

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BY FACSIMILE
00 4989 2399 4465

Our ref.: AT-BF-X11031DIV2-EP
Your ref.:
22 January 2015

Confirmation only
already sent by fax

Dear Sirs,

Re.: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

In connection with the above European patent application and further to your communication under Rule 19 (1) EPC dated 9th January 2015, we can confirm that the correct address for Jon Howarth is:

3804 Vader Drive
Modesto
CA 95356
USA

Please can you correct the inventor details on the EPO Register going forward.

Yours faithfully,
BAILEY WALSH & CO LLP

A. Tomkinson

Also at 20 Bootham, York, YO30 7BL, UK **Tel:** 0800 783 7623
3M Buckley Innovation Centre, Firth Street, Huddersfield, HD1 3BD, UK **Tel:** 0800 783 7623
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ABSTRACT / ZUSAMMENFASSUNG / ABRÉGÉ

14185786.2

Methods for the generation of a peroxyacetic acid sanitizer in proximity to the point-of-use are dis-closed. These methods comprise introducing a hydrogen peroxide precursor solution to water, mixing and then adding an aqueous source of a alkali metal or earth alkali metal hydroxide. Triacetin is a preferred acetyl precursor and is converted rapidly and with a high conversion rate into peracetic acid. These methods produce solutions with a high level of peracetic acid. Methods for preparing then hydrogen peroxide-acetyl precursor solution are also provided.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 317

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P.B. Dyson, LLB (Hons), ACIS, MITMA
A. Tomkinson, MA (Cantab) PhD, CPA, EPA
Associates: P. Stephenson, MSci, PhD, MRSC, CPA, EPA
M. Kellett, MITMA
D. Corbyn, MChem, EPA

European Patent Office
Erhardstrasse 27
D-80298 Munich
Germany

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A. Tomkinson, MA (Cantab) PhD, CPA, EPA
Associates: P. Stephenson, MSci, PhD, MRSC, CPA, EPA
M. Kellett, MITMA
D. Corbyn, MChem, EPA

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00498923994465

Our ref: X11031DIV2-EP
14 January 2015

Dear Sirs

Re: European Patent Application No. 14185786.2 in the name of Enviro Tech Chemical Services, Inc. --Methods and compositions for the generation of peracetic acid on site at the point- of- use

Would you please deduct **€810** from our Account No. 28050202 in payment of the 5th annuity due on the above application before the end of March 2015.

Yours faithfully
BAILEY WALSH & CO. LLP
Bailey Walsh + Co

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EP 14185786.2

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Code		Amount/EUR	Code		Amount/EUR
001	Filing fee – EP direct[3]		010	Opposition fee	
501	Additional fee (more than 35 pages)		011	Fee for appeal	
020	Filing fee – entry EP phase[3] (Rule 159(1)(c) EPC)		029	Certified copy of application; priority document	
520	Additional fee (more than 35 pages) – entry EP phase		033	Renewal fee for the 3rd year	
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002	Fee for a European search		035	Renewal fee for the 5th year	810.00
055	Additional copy of docs cited in search report		036	Renewal fee for the 6th year	
015	Claims fee(s) (Rules 45(1), 162(1)EPC)[5]			Validation for[8]	
005	Designaton fee(s)[4]				
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122	Fee for further processing (non-fee related cases)				
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007	Fee for grant and printing or fee for grant incl. fee for publcation[6]				
008	Additional printing fee for 36th and each subsequent page[7]				
016	Claims fee according to Rule 71(6) EPC[5]				
121	Fee for further processing (late performance of acts R.71(3))				
022	Registering of transfer				

Notes 1 - 9 see overleaf.

Total 810.00

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Bailey Walsh + Co

Place, Date

Leeds, UK; 14 January 2015

EPO 1010 04.14

Bailey Walsh & Co

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A. Tomkinson, MA (Cantab) PhD, CPA, EPA
Associates: P. Stephenson, MSci, PhD, MRSC, CPA, EPA
M. Kellett, MITMA
D. Corbyn, MChem, EPA

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16 Jan. 15

Dear Sirs,

Re.: Courier Records Batch 516

Please find enclosed the documents detailed below with the couriered copy of this faxed cover letter.

Our Ref	Application No.	Document Type	No. Pages	Fee Codes	Total Fee
X11031DIV2-EP	14185786.2	5th Annuity Fee	2	035	€810.00
X11031DIV1-EP	14185791.2	5th Annuity Fee	2	035	€810.00
X11031-EP	11861339.7	5th Annuity Fee	2	035	€810.00
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Also, please note that the faxed copy of this letter is for our information only, so that a fax confirmation is generated for our records.

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Application No.: 14185786.2

The search has started on 15.01.15 (see Notice from the European Patent Office dated 03/2013, OJ EPO 2013, 153).

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M. Kellett, MITMA
D. Corbyn, MChem, EPA

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14 January 2015

Dear Sirs

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Yours faithfully
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	Validation for[9]	
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Notes 1 - 9 see overleaf.

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Place, Date: Leeds, UK; 14 January 2015

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Tomkinson, Alexandra
Bailey Walsh & Co LLP
1 York Place
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ROYAUME UNI

Date
09.01.15

Reference	Application No./Patent No.
AT-BF-G49415	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Communication pursuant to Rule 19(1) EPC

The communication issued pursuant to Rule 19(3) EPC, sent to the inventor designated below, has been returned by the postal services.
You are requested to indicate the correct address of the inventor (R. 19(1) EPC).

Inventor : Howarth, Jonathan . N.
1848 Scenic Drive,
US / Modesto, CA 95355

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Clean Chemistry v. EnviroTech
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Howarth, Jonathan . N.
1848 Scenic Drive,
Modesto, CA California CA95355
ETATS-UNIS D'AMERIQUE

Date
14.11.14

Reference	Application No./Patent No.
	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Designation as inventor - communication under Rule 19(3) EPC

You have been designated as inventor in the above-mentioned European patent application. Below you will find the data contained in the designation of inventor and further data mentioned in Rule 143(1) EPC:

DATE OF FILING : 24.03.11

PRIORITY : / /

TITLE : Methods and compositions for the generation of peracetic acid on site at the point-of-use.

DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

INVENTOR (PUBLISHED = 1, NOT PUBLISHED = 0):

1/Harvey, Michael .S./712, Faust Road/Modesto, CA California CA95358/US
1/Howarth, Jonathan . N./1848 Scenic Drive,/Modesto, CA California CA95355/US

DECLARATION UNDER ARTICLE 81 EPC:
The applicant(s) has (have) acquired the right to the European patent as employer(s).

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Date
14.11.14

Reference	Application No./Patent No.
	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

Designation as inventor - communication under Rule 19(3) EPC

You have been designated as inventor in the above-mentioned European patent application. Below you will find the data contained in the designation of inventor and further data mentioned in Rule 143(1) EPC:

DATE OF FILING : 24.03.11

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TITLE : Methods and compositions for the generation of peracetic acid on site at the point-of-use.

DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

INVENTOR (PUBLISHED = 1, NOT PUBLISHED = 0):

1/Harvey, Michael .S./712, Faust Road/Modesto, CA California CA95358/US
1/Howarth, Jonathan . N./1848 Scenic Drive,/Modesto, CA California CA95355/US

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712, Faust Road
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Date
14.11.14

Reference	Application No./Patent No.
	14185786.2 - 1454
Applicant/Proprietor	
Enviro Tech Chemical Services Inc.	

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PRIORITY : / /

TITLE : Methods and compositions for the generation of peracetic acid on site at the point-of-use.

DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

INVENTOR (PUBLISHED = 1, NOT PUBLISHED = 0):

1/Harvey, Michael .S./712, Faust Road/Modesto, CA California CA95358/US
1/Howarth, Jonathan . N./1848 Scenic Drive,/Modesto, CA California CA95355/US

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Abstract

Methods and compositions for the generation of a peroxyacetic acid sanitizer in proximity to the point-of-use are dis-closed. These methods comprise introducing a hydrogen peroxide precursor solution to water, mixing and then adding an aqueous source of a alkali metal or earth alkali metal hydroxide. Triacetin is a preferred acetyl precursor and is converted rapidly and with a high conversation rate into peracetic acid. These methods produce solutions with a high level of peracetic acid. Methods for preparing then hydrogen peroxide-acetyl precursor solution are also provided. Also disclosed are solid compositions comprising a liquid acetyl precursor, a water-soluble source of hydrogen peroxide, and a water-soluble source of alkalinity. The solid composition is a freely-flowable solid that is used as a agent and a stain remover for the treatment of articles such as fabrics, dentures, textile garments, and equipment used in the food and beverage industry.

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Acknowledgement of receipt

We hereby acknowledge receipt of your request for grant of a European patent as follows:

Submission number	3014653
Application number	EP14185786.2
File No. to be used for priority declarations	EP14185786
Date of receipt	22 September 2014
Your reference	AT-BF-G49415
Applicant	Enviro Tech Chemical Services Inc
Country	US
Title	Methods and Compositions for the generation of peracetic acid on site at the point-of-use.

Documents submitted	
package-data.xml	ep-request.xml
application-body.xml	ep-request.pdf (5 p.)
SPECEPO-2.pdf\X11031-EP Abstract.pdf (1 p.)	SPECEPO-3.pdf\X11031-EP Figures.pdf (1 p.)
SPECEPO-4.pdf\G49415-claims clean.pdf (3 p.)	SPECEPO-1.pdf\X11031-EP Spec 01.pdf (59 p.)
f1002-1.pdf (1 p.)	f1002-2.pdf (1 p.)

Submitted by	CN=Alexandra Tomkinson 4603
Method of submission	Online
Date and time receipt generated	22 September 2014, 15:42 (CEST)

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IPR2025-01471 – Page 332

Message Digest	09:9B:83:13:1A:C9:C9:8E:6A:CF:15:A9:7B:6F:12:4B:30:92:D9:3A

Correction by the EPO of errors in debit instructions filed by eOLF
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/European Patent Office/

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
IPR2025-01471 – Page 333

CLAIMS

1. A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing triacetin and aqueous hydrogen peroxide to the water;

c. mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;

d. adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and

e. forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

2. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced simultaneously.

3. The method of claim 1, wherein the triacetin and the aqueous hydrogen peroxide are introduced sequentially with either one first.

4. The method of claim 1, wherein the provided water is an aqueous stream.

5. The method of claim 1, wherein the provided water is contained in a mixing tank or other vessel.

Petitioner's Exhibit 1022
Clean Chemistry v. EnviroTech
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6. The method of claim 1, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

7. The method of claim 6, wherein the sodium hydroxide is about 1.82% to about 7.28%.

8. The method of claim 1, wherein step (d) is performed simultaneously with step (b).

9. The method of claim 1, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid.

10. The method of claim 9, wherein the time to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid is about 30 seconds to about five minutes.

11. The method of claim 10, wherein the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

12. The method of claim 6, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

13. The method of claim 1, wherein said steps (a) through (e) are performed on a continuous basis.

14. The method of claim 1, wherein said steps (a) through (e) are performed on an intermittent basis.

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METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE

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FIELD OF THE INVENITON

[0001] The invention relates to liquid compositions and methods of using the liquid compositions for the generation of a peroxyacetic acid sanitizer on site in proximity to the point-of-use. The invention also relates to a solid bleaching and stain removal composition.

BACKGROUND OF THE INVENTION

[0002] **A. Liquid PAA Disinfectants and Sanitizers**

[0003] Disinfectants and sanitizers based on peroxyacetic acid (PAA), also commonly known as peracetic acid, are used in the dairy, food and beverage processing industries for clean-in-place pipeline and equipment disinfecting and cleaning, for fruit and vegetable washing, and in the treatment of meat, poultry and seafood products. Peroxyacetic acid disinfectants are also used in the treatment of cooling water, process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0004] Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene

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diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pails, in preparation for shipment to the end user. Typical commercial products have concentrations of PAA of about 1-15% w/w, although a concentration of up to 30% is possible. However, the latter concentration product only finds captive use because of its extremely hazardous and explosive properties.

[0005] There are several problems with the use of equilibrium solutions of PAA. First, the low concentration of PAA (1-15%) means that most of the weight (85-99%) of the products consist of substantial amounts of inert ingredients, such as water, acetic acid, and hydrogen peroxide. This results in the need for larger product storage areas and causes increased transportation and handling costs. Second, the products are inefficient in the use of both hydrogen peroxide (hydrogen peroxide) and acetic acid (AA). To maintain adequate storage stability of the PAA, either hydrogen peroxide or AA must be present at a level on a weight percentage basis that is greater than the level of PAA, which increases raw material costs. Third, the presence of the HEDP or dipicolinic acid stabilizer limits the amount of PAA that can be applied to certain foodstuffs because the amount of HEDP or dipicolinic acid is regulated by the Food and Drug Administration (FDA). Fourth, the reaction between hydrogen peroxide and AA is quite slow in some cases, and typically requires several days' time before the PAA product can be tested for quality confirmation. Therefore, manufacturers of these products must store large inventories of the PAA product before it can be shipped to the end user. Fifth, for transportation purposes, equilibrium solutions that are greater than 6% PAA are considered to be dangerous products and must be labeled with the DOT marking "Organic Peroxide", Hazard Class 5.2, 8 (oxidizer, corrosive). If producers and end-users exceed the yearly threshold amount of just 6,666 lbs. of 15% PAA, they must file Risk Management Plans with both federal EPA and state

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authorities. This is an arduous and time-consuming process. In addition, producers of equilibrium solutions of PAA that are over 6% PAA must obtain permitting by the local fire department and pay an extra hazardous material shipping fee when the product is shipped from their facility. On the other hand, there are much less stringent requirements for products that contain hydrogen peroxide, and all reporting, permitting and shipping restrictions are lifted for products that contain less than 27% hydrogen peroxide.

[0006] As a result of these problems, there have been various attempts to make non-equilibrium solutions of PAA on site, at the point-of-use. For example, U.S. patent no. 7,012,154 discloses a system in which AA, hydrogen peroxide, water, and sulfuric acid are fed to a jacketed reactor for the production of PAA. A wiped-film distillation column attached to the reactor condenses and isolates the pure PAA from the gas phase and immediately introduces it to the receiving water. This system suffers from a number of drawbacks. First, it is extremely capital intensive due to the high cost of the equipment, including the reactor, heater, pumps, distillation column, and computerized control system which ensures accurate metering of the reagents. Second, there are significant safety hazards associated with the production of pure PAA due to its explosive properties. Third, the equipment and synthesis process is very complex and requires knowledgeable and highly trained technicians to continuously operate and maintain the system in a safe and effective manner.

[0007] Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. patent nos. 6,171,551 and 6,387,236 disclose processes that employ a cell divided by an ion-exchange membrane in which PAA (and other oxidants including hydrogen peroxide and ozone) are produced in the anode compartment which consists of an aqueous solution of acetic acid or acetate salt. In addition to the high costs of electricity and electrolysis equipment, these processes also result in a very low yield of PAA from the

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acetyl precursor. For example, the '551 patent reports that less than 14 ppm of PAA was produced after 90 minutes of electrolysis of a 490,000 ppm anolyte of aqueous potassium acetate. In addition, these processes are difficult to perform intermittently.

[0008] Other methods of generating non-equilibrium solutions of PAA on site, using electrolysis, are described in WIPO International Publication Nos. WO 2004/0245116 and WO 2008/140988, and U.S. Patent Application Publication No. 2009/0314652. These references disclose cation membrane-divided electrolysis cells and the use of gas diffusion electrodes to effect the cathodic reduction of oxygen gas to hydrogen peroxide under alkaline conditions. The hydrogen peroxide was then allowed to react with acetic acid or an acetyl precursor to form PAA in the bulk solution, whereupon the catholyte was directed to the acidic anode compartment of the cell to stabilize the PAA. This system suffers from several disadvantages. Due to the low solubility of oxygen in water (about 8 ppm maximum), the concentration of electroactive species is very low, which forces the cell to operate at low current density (amperage per surface area of electrode). In order to produce a meaningful amount of hydrogen peroxide, the cells must have a very large surface area. This requires high capital equipment costs and a very large footprint for the electrolysis equipment. Another disadvantage of this system is that it is very difficult to maintain steady-state conditions and simultaneously balance the feed of acetic acid or acetyl precursor to the cathode compartment with the concurrent withdrawal of acidified PAA solution from the anode compartment. This is because cations carrying the cell current through the cation exchange membrane are always hydrated so as the cations move through the membrane, they are accompanied by water molecules. As a result, the volume of the anolyte decreases and the volume of the catholyte increases, making the steady-state condition difficult to maintain. It is difficult to perform this process intermittently. Finally, this system can only be of economic value if the source of oxygen is air, which comprises 23% oxygen. However, the carbon dioxide

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contained in air causes carbonates to precipitate, which impedes the flow of electrical current, limiting or eliminating the production of hydrogen peroxide, and hence, PAA.

[0009] Another method of making a non-equilibrium solution of PAA at the point-of-use is disclosed in WIPO International Publication No. WO 2008/140988 and U.S. Patent Application Publication Nos. 2009/0005590 and 2007/0082832. These references disclose biosynthetic methods of producing peracids from carboxylic acids and carboxylic acid esters. These methods involve the use of perhydrolase enzymes to catalyze the perhydrolysis of the carboxylic acid or ester into the peracid using a solid or liquid source of hydrogen peroxide. Although these methods can produce compositions containing up to 20 parts of peracid to one part of hydrogen peroxide, they are limited by the amount of peracid that can be produced before the perhydrolase enzyme is oxidized by the reactant products and ceases to function as intended. The highest concentration of peracid disclosed by these references was 0.16% (1,600 mg/L). However, peracid or PAA solutions that are produced with enzymes have limited appeal because they are very expensive to produce, and for regulatory reasons, the enzyme must be removed from the solution before the solution can be applied to food or hard surfaces for disinfection purposes. Removing the enzyme from the solution is not an easy task; thus, it is typically not done. Therefore, PAA solutions prepared by enzymatic methods are not suitable for the more broad commercial uses in the food, dairy, beverage, meat, and poultry industries, which are regulated by the FDA and the Environmental Protection Agency (EPA).

[0010] Another method of generating non-equilibrium PAA at its point-of-use requires substituting the traditional mineral acid catalyst with sulfonic acid ion-exchange resins, as disclosed in U.S. patent no. 5,122,538. A solution containing a 1.5:1 mole ratio of AA to hydrogen peroxide was passed through a column packed with a sulfonic acid ion-exchange resin and produced a solution of 15% PAA within 30 minutes. The method described in the '538

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patent suffers from the limitation that it requires a large volume of expensive resin bed in order to be effective. Moreover, all existing ion exchange resin systems are limited by the fact the resin is subject to oxidative degradation by PAA and have a short limited lifespan.

[0011] Other attempts to produce non-equilibrium PAA solutions on site, at the point-of-use, for bleaching cellulosic materials have reacted hydrogen peroxide with acetic anhydride. For example, U.S. patent no. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium hydroxide catalyst were metered to a tubular reactor to continuously produce a solution containing 3.25% PAA with a conversion of 78% hydrogen peroxide. However, the process generated measurable amounts of diacetyl peroxide (0.44%) which is an explosion hazard. Moreover, the reaction product would be unsuited for any application other than cellulosic bleaching purposes because there was no attempt to remove the ammonium hydroxide catalyst from the reaction medium. Ammonium hydroxide is an undesirable contaminant in PAA products that are used as disinfectants and sanitizers in the dairy, food, and beverage processing industries, and in PAA products used in fruit and vegetable washing and in the treatment of meat, poultry, and seafood.

[0012] Another process for generating non-equilibrium solutions of PAA on site, at the point-of-use was disclosed in U.S. Patent Application Publication No. 2009/0043132. This process utilized introduction of hydrogen peroxide into a sidestream of the water requiring treatment. This was followed by introducing acetic anhydride, whereupon PAA was generated *in-situ*. It was found that acetic anhydride preferentially reacted with hydrogen peroxide rather than undergo undesirable hydrolysis with water. Within 20 minutes, up to 3000 ppm of PAA was generated in the sidestream which was then reconstituted with the main body of water and diluted further. All processes that employ acetic anhydride suffer the limitation that acetic anhydride is expensive, very corrosive, an irritant, and highly flammable.

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[0013] Yet another process for generating non-equilibrium solutions of PAA on site at the point-of-use is disclosed in WIPO International Publication No. WO 01/46519 A1. This process utilized the metering of an aqueous solution of hydrogen peroxide into an agitated tank and co-metering a solid dry source of tetraacetylethylenediamine (TAED) from a storage hopper using a screw feeder. The agitator kept the solid TAED suspended in the hydrogen peroxide solution which was then fed to an in-line static mixer where aqueous sodium hydroxide was introduced. The mixture was then directed through 200 meters of coiled tubing immersed in a cooling tank so that the temperature rise accompanying the exothermic reaction was contained. Upon exiting the coiled tubing, the mixture containing PAA could be directed to the water requiring treatment. Disadvantages of this approach include the difficulty of accurately metering a solid and a liquid simultaneously, and the high capital equipment cost of the metering system, electronic controllers, agitation tank, coiled tubular reactor, and the cooling system.

[0014] Thus, there is a need for a method to make non-equilibrium PAA on site at the point-of-use that addresses the above problems.

[0015] **B. Solid PAA Bleaches and Stain Removers**

[0016] PAA is also used in laundry bleaching applications where it is generated *in-situ* in the laundry wash water. The PAA is typically produced from a solid source of hydrogen peroxide, such as sodium percarbonate or sodium perborate. The hydrogen peroxide must be in the presence of a solid acetyl precursor, most typically, tetraacetylethylenediamine (TAED). When dissolved in laundry wash water, the TAED undergoes a perhydrolysis reaction with hydrogen peroxide to form PAA. TAED is the preferred acetyl precursor because it possesses low toxicity, is of low environmental impact, and is readily biodegradable. However, TAED-based laundry bleaches have several problems. First, of the four acetyl groups on TAED, only two are known to be available for perhydrolysis, making TAED an expensive acetyl precursor on

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a weight basis. Second, TAED has low water solubility, especially at the cooler water temperature bleaching cycles that are less damaging to fabrics. This is a major drawback, as current consumer trends in energy conservation are towards bleaching laundry fabrics with cool temperature water, rather than heated water. Undissolved TAED in cool temperature water is less unavailable as an acetyl precursor for the dissolved source of hydrogen peroxide and can even deposit on fabrics, necessitating a separate rinse step to remove it. Third, over time, when exposed to high humidity, solid TAED can react with the solid source of hydrogen peroxide and the free water to form PAA, as well as degrade the activity, making it less effective over time. Because the PAA is volatile, it imparts an undesirable pungent odor to the product. Thus, there is a need for a solid, peroxygen bleach that overcomes the deficiencies of the TAED-containing bleaches.

SUMMARY OF THE INVENTION

[0017] In an embodiment, liquid compositions for use in generating non-equilibrium solutions of PAA are provided. These hydrogen peroxide-acetyl precursor solutions comprise a solution of aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water. A preferable acetyl precursor is triacetin, which displays an unexpectedly high solubility in hydrogen peroxide. These hydrogen peroxide-acetyl precursor solutions may be used for generating a non-equilibrium solution of peracetic acid for use as a disinfectant or sanitizer on a site having a point-of-use of peracetic acid.

[0018] The hydrogen peroxide-acetyl precursor solutions are advantageous in that they are formulated such that sufficient acetyl precursor can be dissolved in an amount of hydrogen peroxide that would fully perhydrolyze all of the acetyl groups of the acetyl precursor.

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Moverover, the hydrogen peroxide component of these compositions is remarkably stable. These compositions overcome one or more problems of the known prior art, and are free of the regulatory reporting, permitting, and shipping restrictions that govern equilibrium PAA products.

[0019] In another embodiment, a method of preparing a hydrogen peroxide-acetyl precursor solution is provided. The method comprises introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

[0020] A further embodiment is a method of continuously or intermittently generating a non-equilibrium solution of peracetic acid on a site having a point-of-use of peracetic acid for use as a disinfectant or sanitizer. Water is provided on the site having the point-of-use. The water may be a flowing aqueous stream or it may be contained in a mixing tank or other vessel. A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use. In one embodiment, the liquid acetyl precursor is triacetin and the solution that is formed is a hydrogen peroxide-triacetin solution. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and then used to prepare the hydrogen peroxide-acetyl precursor solution on the site. The hydrogen peroxide-acetyl precursor solution is then introduced to the water. Alternatively, and in another embodiment, the acetyl precursor and the aqueous hydrogen peroxide may be introduced to the water separately, either sequentially, with either one first, or simultaneously. The hydrogen peroxide-acetyl precursor solution and the water are mixed to form a mixture. An aqueous source of an alkali metal or earth alkali metal hydroxide, such as sodium hydroxide, is provided on the site having the point-of-use. The aqueous source of an alkali metal or earth alkali metal

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hydroxide is added to the mixture. Alternatively, and in another embodiment, the aqueous source of alkali metal or earth alkali metal hydroxide may be added simultaneously with the hydrogen peroxide-acetyl precursor solution or with the acetyl precursor and the aqueous hydrogen peroxide, to the water. A reaction medium comprising a non-equilibrium solution of peracetic acid is formed. In the reaction medium, the hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Almost instantaneously, a non-equilibrium solution of PAA is formed. Within about 30 seconds to about five minutes, the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid is maximized. When triacetin is used as the acetyl precursor and assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into peracetic acid, and the percent of hydrogen peroxide remaining is about 0.078% to about 1.88%. The reaction medium may optionally be sampled at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

[0021] The non-equilibrium solutions of PAA that are formed comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. The peracetic acid solutions are alkaline, having a pH of about 11.2 to about 13.37. The reaction is remarkably fast, proceeds with a high conversion of the acetyl precursor into PAA. This method produces solutions with a high level of PAA, from about 1% to about 7.1%.

[0022] The PAA solution is introduced to the receiving water at the point-of-use. It may be introduced immediately, or stabilized with the addition of a source of acid and used throughout a working day. The receiving water may be water used in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and

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vegetable washing; and in the treatment of meat, poultry, and seafood products. The receiving water may also be cooling water, oil and gas process water, or municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[0023] This method addresses one or more problems of the known prior art. The method is easy to perform, inexpensive to operate, and requires only basic and common equipment. The method is safe, in that it does not isolate pure PAA, and there is no possibility of a catastrophic event due to an equipment failure, such as over-pressurization or explosions. When triacetin is used as the acetyl precursor, it is inexpensive, non-toxic, safe, non-corrosive, non-irritating, non-flammable, sanctioned as Generally Recognized as Safe (GRAS) by the FDA, and converted quickly and with a high conversion rate into PAA. The method does not require the use of perhydrolase enzymes, acetic acid, or acetic anhydride, all of which suffer from the aforementioned limitations and problems. The method generates a PAA product that does not contain ammonium hydroxide. The method can be performed to generate a PAA product in a continuous or intermittent fashion. Further, the method allows the end-user the choice of utilizing the on site generated PAA immediately or later over the course of a working day.

[0024] In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided. The solid composition comprises a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. The liquid acetyl precursor is preferably triacetin The composition produces peracetic acid upon being introduced to water. Upon dissolution, the solid hydrogen peroxide source releases hydrogen peroxide and the solid source of alkalinity dissolves to increase the pH, resulting in the formation of peracetic acid from the reaction of the hydrogen peroxide and the acetyl precursor.

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[0025] The solid composition is used as a bleaching agent and a stain remover for the treatment of articles such as fabrics, dentures, textile garments, and equipment used in the food and beverage industry. The solid composition is advantageous in that it does not give rise to an undesirable PAA odor upon storage, contains an acetyl precursor that efficiently utilizes the acetyl groups it contains, and has a high solubility in cool temperature water which quickly and efficiently produces PAA without the need for elevated water temperatures. Moreover, the acetyl precursor used in making the solid composition may also be used in preparing the liquid compositions described in section 3 above, streamlining manufacturing practices by using the same acetyl precursor as an ingredient in liquid as well as solid compositions.

[0026] Surprisingly, this freely-flowable, solid composition includes a liquid acetyl precursor, triacetin. In addition, it is surprising that this composition does not produce a strong odor of peracetic acid during storage.

[0027] In another embodiment, a method of preparing the freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided.

BRIEF DESCRIPTION OF THE DRAWING

[0028] Figure 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point-of-use of peracetic acid In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.

DETAILED DESCRIPTION OF THE INVENTION

[0029] 1. **Definitions**

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[0030] The terms "PAA" and "peracetic acid" mean peroxyacetic acid or peracetic acid, and/or the conjugate base of peracetic acid (the peracetate ion).

[0031] The terms "percent" and "%" mean weight percent, except when referring to the percent converted.

[0032] The term "receiving water" means the water that is being treated.

[0033] The term "point-of-use" means the location where the peracetic acid enters the receiving water.

[0034] 2. **Experimental Methods**

[0035] PAA and hydrogen peroxide in solution were determined using the ceric sulfate-sodium thiosulfate method. The method involves adding a known weight of sample containing the PAA and hydrogen peroxide (or dilution) to a beaker containing 50 ml of chilled 0.9 N sulfuric acid. Using a transfer pipette, 1-2 grams is accurately weighed to a sample cup and reverse osmosis (RO) or deionized water is added to provide a workable volume. Five drops of ferroin indicator is then added with stirring, and the sample is then titrated with 0.1 N ceric sulfate until the sample turns from purple to blue. The volume of ceric sulfate required in mL is recorded. Then, one or two small scoops of potassium iodide are added to the sample cup, which turns the solution dark brown. The sample is then titrated with 0.1 N sodium thiosulfate to discharge the brown coloration and form a pale straw coloration. Then, 10-15 drops of 0.5% starch indicator solution is introduced and the sample turns blue-black. The sodium thiosulfate is then added dropwise until the color transitions to a bright orange. The volume of sodium thiosulfate in mL was recorded. The percent hydrogen peroxide and the percent PAA are calculated as follows:

$$\% \text{ hydrogen peroxide} = \frac{\text{mL 0.1 N ceric sulfate} \times 0.17}{\text{wt. sample}}$$

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$$\% \text{ PAA} = \frac{\text{mL 0.1 N sodium thiosulfate} \times 0.38}{\text{wt. sample}}$$

[0036] For kinetic runs which involved measuring the PAA and hydrogen peroxide in samples at one, three, and five minute intervals after adding the reactants together, the generation reaction was quenched by adding a sample of the reaction medium to the sulfuric acid. This halted the generation reaction and stabilized the PAA and hydrogen peroxide to elevated pH degradation reactions. This permitted the samples to be taken at the appropriate time interval (one, three, and five minutes), and analyzed later.

[0037] In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. patent no. 7,651,724) was employed. This analytical technique is based on a modified DPD (N,N-diethyl-*p*-phenylenediamine) colorimetric method accepted by the EPA for measuring total chlorine in drinking water and wastewater. It relies on the ability of PAA to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I^-) into iodine (I_2) that reacts with a color indicator (DPD), which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl_2. A calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl_2 (76/71 = 1.07).

[0038] Hydrogen peroxide does not interfere with the measurement for PAA provided the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen peroxide to be measured, it must be activated by addition of a sodium molybdate catalyst and then given time (six minutes) to react with the I^- ion to liberate I_2. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the

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sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2. After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2 (34/71 = 0.479).

[0039] 3. **Liquid Compositions for Generating Non-Equilibrium Solutions of PAA On a Site Having a Point-of-Use**

[0040] In an embodiment, liquid compositions for generating non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid are provided. These solutions are referred to as "hydrogen peroxide-acetyl precursor solutions." These solutions comprise aqueous hydrogen peroxide, a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide, a trace amount of peracetic acid, and water.

[0041] The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

[0042] (a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.

[0043] Triacetin is a preferable liquid acetyl precursor and 50% hydrogen peroxide is a preferable solution of aqueous hydrogen peroxide. The triacetin is preferably added to the 50% hydrogen peroxide at room temperature. Alternatively, 70% hydrogen peroxide can be used, but it is not widely available and requires special handling and transportation. Given that the solubility of triacetin in water is only 7% at 25°C, triacetin is unexpectedly highly soluble in 50% hydrogen peroxide. It solubilizes without an exotherm (temperature increase).

[0044] The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

[0045] (b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

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[0046] The solution is mixed until a homogenous solution has been formed. The solution is allowed to mix by diffusion or by using a mixing device that is suitable for mixing liquids together. For example, 50% hydrogen peroxide can be introduced to a batch tank equipped with an overhead agitator blade. Triacetin can then be introduced to the 50% hydrogen peroxide when the agitator is in motion so that the components are thoroughly mixed.

[0047] The solution that is formed is a hydrogen peroxide-acetyl precursor solution, which also includes varying amounts of water, depending on the formulation used. When triacetin is used as the liquid acetyl precursor, the solution that is formed is a hydrogen peroxide-triacetin solution. One such hydrogen peroxide-triacetin solution comprises about 23% to about 40% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 20% to about 52% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor solution. The pH is about 1.46 to about 2.2 and no deliberate attempt is made to adjust the pH further.

[0048] A preferable hydrogen peroxide-triacetin solution comprises about 27.15% hydrogen peroxide (from 50% aqueous hydrogen peroxide), about 45.67% triacetin, water, and a trace amount of PAA that is formed within the first day of preparing the hydrogen peroxide-acetyl precursor solution. The mole ratio of hydrogen peroxide:triacetin is about 3.8:1.

[0049] The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

[0050] Example 1

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[0051] Triacetin (83.05 g) was added to 50% hydrogen peroxide solution (75 g) to form 158.05 g of a mixture. There was no evolution of gas indicating the hydrogen peroxide had decomposed to oxygen, nor was there any exotherm indicating that a chemical reaction had occurred. The solution did not turn oily or cloudy but remained clear. The solution was calculated to comprise 23.73% hydrogen peroxide and 52.55% triacetin, with the balance being water, and had a measured pH of 2.2. The mole ratio of hydrogen peroxide to triacetin was calculated to be 2.98:1. Titration of the solution immediately upon preparation yielded 24.1% hydrogen peroxide, which is within experimental error of the calculated amount of hydrogen peroxide.

[0052] This experiment showed that triacetin is remarkably soluble in 50% hydrogen peroxide. The solubility of triacetin was found to be at least 52.55%. This is surprising, given that the solubility of triacetin in water is only 7% at 25°C.

[0053] In order to test the stability of the mixture, the amount of hydrogen peroxide remaining and the amount of PAA generated was tracked for several months. The mixture was held at ambient temperature away from sources of light. Table I summarizes the data.

[0054] Table I

Day #	% Hydrogen Peroxide Remaining	% PAA Generated
1	23.79	0.00
29	23.32	1.28
57	22.56	2.36
92	21.06	4.22
120	19.54	6.05
134	18.57	6.87

[0055] Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had

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lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

[0056] Example 2

[0057] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 12.84:1 was prepared by adding triacetin (100.0 g) to 50% hydrogen peroxide (400.0 g) so that the mixture was 40% hydrogen peroxide and 20% triacetin, with the balance being water. The pH of the solution was 1.46 and the pH of a 1:100 dilution was 3.69. To accelerate storage characteristics, the sample was placed in an incubator set for 86-87° F. Table II shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of more than six months.

[0058] Table II

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	40.21	0.004
33	38.02	3.499
54	35.5	5.992
96	29.27	8.36
127	25.05	6.66
173	18.49	4.43
201	15.67	3.51

[0059] Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen

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peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

[0060] Example 3

[0061] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin (37.5008 g) to 50% hydrogen peroxide (65.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

[0062] Table III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

[0063] In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

[0064] Example 4

[0065] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample

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was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

[0066] Table IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

[0067] Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

[0068] Example 5

[0069] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 4.8:1 was prepared by adding triacetin (37.50 g) to 50% hydrogen peroxide (56.25 g) so that the mixture was 30% hydrogen peroxide and 40% triacetin, with the balance being water. The pH of the solution was 1.67 and the pH of a 1:100 dilution was 4.62. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table V shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 43 days.

[0070] Table V

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	30.08	0.38
8	29.85	0.784
15	29.63	1.22
22	29.37	1.71
29	28.76	2.26
36	28.67	2.78
43	28.31	3.41

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[0071] Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

[0072] Example 6

[0073] A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.

[0074] Table VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

[0075] Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.

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[0076] Example 7

[0077] A 30-gallon batch of 50% hydrogen peroxide and triacetin was prepared by blending 137 lbs triacetin with 163 lbs 50% hydrogen peroxide so that the mixture was 27.15% hydrogen peroxide and 45.67% triacetin, with the balance being water. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The mixture was stored in an opaque drum in a non-climate controlled environment. On storage, the mixture slowly formed PAA in the container. Since this reaction of hydrogen peroxide to PAA does not represent a destructive loss of total peroxygen, to determine the true stability of the hydrogen peroxide, both the hydrogen peroxide and the peracetic acid generated must be quantified and reported as total peroxygen recovered.

[0078] After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate–iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.

[0079] Table VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

[0080] After 295 days, 22.17% of the total peroxygen was recovered as either titratable hydrogen peroxide or hydrogen peroxide reacted to form PAA. To determine the stability of the peroxygen in the mixture, the total recovered hydrogen peroxide after 295 days (22.17%) was

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subtracted from the total recovered hydrogen peroxide of the initial theoretical value (27.17%). The result, 5%, is the loss of peroxygen (expressed as hydrogen peroxide) after 295 days of storage in a non-climate controlled environment.

4. Methods of Generating Non-Equilibrium PAA On Site at the Point-of-Use

[0081] Methods of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use of PAA for use as a disinfectant or sanitizer, using a source of water that is an aqueous stream or by a batch process using water in a container, are provided.

[0082] In one embodiment, a method of continuously or intermittently generating non-equilibrium solutions of PAA on a site having a point-of-use, using a source of water that is an aqueous stream, comprises the following steps.

[0083] (a) Providing water.

[0084] Flowing water is provided on a site having a point-of-use of peracetic acid.

[0085] The water may be flowing in, for example, a pipe, a flume, a canal, or other types of aqueous streams. The water pressure should be regulated and the flow rate should be monitored or measured. Any suitable flow meter may be used, such as a rotameter, a magnetic flow meter, an ultrasonic flow meter, a Doppler flow meter, a differential-pressure flow meter, a turbine flow meter, or a Coriolis flow meter.

[0086] The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

[0087] (b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[0088] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be

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prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[0089] A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[0090] The hydrogen peroxide-acetyl precursor solution is introduced to the flowing water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[0091] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the aqueous water stream, for example, through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the pressure of the water flowing in the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump. The rate at which the hydrogen peroxide-acetyl precursor solution is pumped into the flowing water is governed by a controller that is interfaced to a flow meter that is measuring the flow of the water. In this way, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped may be matched to the flow of the water in the aqueous stream. If the flow of the water slows, the rate at which the hydrogen peroxide-acetyl precursor solution is pumped should slow accordingly. If the flow of the water stops, the hydrogen peroxide-acetyl precursor pump should stop.

[0092] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

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[0093] (c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[0094] Any mixing device suitable for mixing liquids may be used. An example is a static mixer located just after the point that the hydrogen peroxide-acetyl precursor solution is introduced to the flowing water. One type of static mixer utilizes a non-moving element such as a series of baffles. As the mixture flows through the static mixer under the motive force of the flowing water, the non-moving element divides the flow several times to provide radial mixing. Another type of static mixer utilizes a series of obstructions, such as column packing or glass beads, provided there is a low differential pressure drop across the mixer. The obstructions provide for turbulent mixing of the hydrogen peroxide-acetyl precursor solution and the flowing water. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed. The velocity of the water will determine the time it takes to complete the mixing and the efficiency of the mixing. For example, with ¾" pipe, a static mixer of ¾" diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

[0095] (d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[0096] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. A preferable aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. Other suitable alkali metal hydroxides include 45% potassium hydroxide.

[0097] Sufficient 50% NaOH is added to the flowing mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. When the acetyl precursor is triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

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[0098] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the pipe. Any suitable pump capable of overcoming the hydraulic pressure of the pipe may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[0099] The rate at which the 50% NaOH solution is pumped into the pipe is governed by the same controller that is interfaced to both the flow meter that is measuring the flow of the mixture and the pump controlling the rate of introduction of the hydrogen peroxide-acetyl precursor solution. In this way, the rate at which the 50% NaOH solution is introduced may be matched to both the flow of the mixture and the rate of introducing the hydrogen peroxide-acetyl precursor solution. If the flow of the mixture slows for any reason, the rate at which the 50% NaOH solution is pumped should slow accordingly. If the flow of the mixture stops, the 50% NaOH pump should stop as well.

[00100] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

[00101] (e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[00102] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[00103] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis

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reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. When the acetyl precursors is triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[00104] This method may also include an optional step after step (e) of sampling the reaction medium at various times after the addition of the aqueous source of alkali metal or earth alkali metal hydroxide to determine the time required under the existing conditions to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into PAA. This may be accomplished by directing the flow of the reaction medium through a series of residence chambers equipped with sampling ports. The residence chambers are designed to be of sufficient volume such that a certain amount of time has elapsed since the introduction of the 50% NaOH. Thus, at any given flow rate in the pipe, the first residence chamber is of a volume such that 30 seconds have elapsed since the introduction of 50% NaOH, one minute has elapsed by the time the flow reaches the sampling port immediately after the second residence chamber, and additional time elapses by the time the flow reaches the remaining sampling ports. Up to four residence chambers and sampling ports may be placed in series such as this to provide the user with about 30 seconds to five minutes of residence time after the introduction of the 50% NaOH. Once the flow of the reaction medium has been established, samples are drawn from all four sampling ports associated with the residence chambers and analyzed for peracetic acid. The sample which registers the highest amount of peracetic acid is deemed to be drawn from the sampling port associated with the residence chamber corresponding to the time of maximum conversion of the acetyl precursor into peracetic acid. At this point, the entire flow of reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

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[00105] In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

[00106] (a) Providing water.

[00107] A container of water, such as a mixing tank or other vessel, is provided on a site having a point-of-use of peracetic acid. The water should be softened, deionized, or of sufficient low hardness that it will not precipitate calcium salts when the alkali metal or earth alkali metal hydroxide is introduced in step (d).

[00108] (b) Introducing a hydrogen peroxide-acetyl precursor solution to the water.

[00109] A hydrogen peroxide-acetyl precursor solution is provided on the site having the point-of-use of the PAA. The hydrogen peroxide-acetyl precursor solution may be prepared by the steps set forth in section 3 above. The hydrogen peroxide-acetyl precursor solution may be prepared off site and then transported to the site having the point-of-use, or the acetyl precursor and the aqueous hydrogen peroxide may be transported to the site having the point-of-use and used to prepare the hydrogen peroxide-acetyl precursor solution on the site.

[00110] A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

[00111] The hydrogen peroxide-acetyl precursor solution is introduced to the water in an amount such that the hydrogen peroxide-acetyl precursor solution is about 5.6% to about 22.5% of the total.

[00112] The hydrogen peroxide-acetyl precursor solution is pumped from its container into the container of water through an injection quill mounted on the side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

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[00113] As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be introduced to the water separately, either simultaneously or sequentially. If they are introduced sequentially, either one may be added first. If the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced separately, rather than as an hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

[00114] (c) Mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture.

[00115] Any mixing device suitable for mixing liquids may be used. An example is an overhead stirrer, such as an agitator blade. The container of water is equipped with a baffle to assist the process of mixing. The mixing should yield a homogeneous solution with no concentration gradients before the next step is performed.

[00116] (d) Adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.

[00117] An aqueous source of an alkali metal or earth alkali metal hydroxide is provided on the site having the point-of-use. A preferable aqueous source of an alkali metal hydroxide is sodium hydroxide, and 50% sodium hydroxide is most preferable. Other suitable alkali metal hydroxides include 45% potassium hydroxide.

[00118] Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28% of the total amount. When the acetyl precursor is triacetin, a preferred mole ratio of NaOH: hydrogen peroxide:triacetin is about 4.2:3.8:1.

[00119] The 50% NaOH solution is added to the mixture by pumping it from its container with a suitable pumping device and into the mixture through an injection quill mounted on the

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side of the container of water. Any suitable pump may be used. Examples include a solenoid-driven or air-driven diaphragm pump or a peristaltic pump.

[00120] Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

[00121] (e) Forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

[00122] The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with the acetyl precursor to form peracetic acid. Depending upon the temperature of the water, the efficiency of mixing, and the mole ratio of NaOH:hydrogen peroxide:acetyl precursor employed, the amount of hydrogen peroxide and acetyl precursor that are converted into PAA is maximized within about 30 seconds to about five minutes.

[00123] The non-equilibrium solutions of PAA prepared by this method comprise PAA, unreacted hydrogen peroxide, unreacted acetyl precursor, the product of the perhydrolysis reaction of the acetyl precursor, the aqueous source of alkali metal or earth alkali metal hydroxide, and water. When the acetyl precursors is triacetin, the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[00124] While not wishing to be bound by theory, it is believed that under elevated pH conditions created by the addition of a source of alkali metal hydroxide or earth alkali metal hydroxide, hydrogen peroxide dissociates according to the following equation:

$$H_2O_2 = H^+ + HO_2^-$$

[00125] The perhydroxyl anion (HO_2^-) then affects nucleophilic substitution reactions on the carbonyl groups of the acetyl precursor in a perhydrolysis reaction to form peracetic acid and the product of the perhydroloysis reaction of the acetyl precursor. When the acetyl precursor is

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triacetin and all three acetyl groups are reacted, then the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

[00126] In these methods, the perhydrolysis reaction is rapid and the maximum amount of PAA is generated within about 30 seconds to about five minutes at ambient temperature. The methods efficiently utilize the acetyl precursor and the source of hydrogen peroxide. When triacetin is used, assuming all three acetyl groups are reacted, about 40.9% to about 85.7% of the triacetin is converted into PAA. The percent of hydrogen peroxide remaining is about 0.078% to about 1.88%.

[00127] The non-equilibrium solutions of PAA prepared by these methods have several unique characteristics. The PAA solutions have high levels of PAA, from about 1% to about 7.1%. In addition, the PAA solutions are alkaline, having a pH of about 11.2 to about 13.37.

[00128] The non-equilibrium solutions of PAA may be immediately introduced to the receiving water at the point-of-use. Alternatively, the solutions may be stabilized by halting the decomposition of the PAA by adding a source of acid to lower the elevated pH of the reaction medium caused by the addition of an alkali metal or earth alkali metal hydroxide, and to provide neutral to mildly acid pH conditions to stabilize the PAA to elevated pH degradation. The acid-stabilized PAA solutions can then be stored and used at the point-of-use as required throughout a working day.

[00129] The non-equilibrium PAA solutions produced by these methods can be advantageously used wherever traditional equilibrium solutions of PAA are used. Thus, the PAA solutions may be used as a disinfectant and sanitizer in the dairy, food, and beverage processing industries for clean-in-place pipeline and equipment cleaning; for fruit and vegetable washing; and in the treatment of meat, poultry, and seafood products. These PAA solutions may also be

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used in the treatment of cooling water, oil and gas process water, and municipal wastewater. Other uses include slime and biofilm removal in papermaking processes.

[00130] For both of the above methods, steps (a) through (e) may be performed on a continuous or intermittent basis. In a continuous basis, the steps are performed under conditions of steady state, and the PAA solution is produced at the same rate as a function of time. However, intermittent performing of steps (a) through (e) is possible if the demand for the PAA solution drops for any reason (e.g., change in working shift or the target level of PAA in the receiving water has been achieved), in which case, steps (a) through (e) may be discontinued and resumed when the demand increases.

[00131] Example 8

[00132] Tests were performed using about one liter of reverse osmosis (RO) or softened water which was buffered to an alkaline pH. The buffering media included 0.1 and 0.2 M Na_2CO_3 solutions, in addition to 0.1 and 0.2 M NaOH solutions. Sufficient buffering media was added to the water in order to achieve the desired pH. The amount of hydrogen peroxide (introduced as 50% hydrogen peroxide) and triacetin used in the tests is summarized in Table VIII. The reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as "double"), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as "mixed"). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate–iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

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[00133] Table VIII

t #	Moles Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)	pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remainin g	% Triacetin Converted to PAA
	4.99	Double	10.50	8.60	5.53	0.170	0.329	29.6%
	5.47	Double	10.50	8.60	5.04	0.178	0.333	33.9%
	5.45	Double	10.80	8.61	5.07	0.192	0.329	36.4%
	5.68	Double	11.00	8.87	5.01	0.201	0.322	38.6%
	5.72	Double	11.00	9.13	5.12	0.068	0.416	12.8%
	5.49	Double	12.42	8.60	5.02	0.169	0.306	32.4%
	5.59	Double	12.91	8.60	4.93	0.320	0.265	62.4%
	5.53	Double	12.80	8.69	5.04	0.335	0.273	63.9%
	25.0	Double	12.65	9.03	1.16	0.104	0.413	85.9%
0	5.26	Double	12.60	8.70	5.30	0.298	0.247	54.1%
1	5.52	Sequential	12.83	8.68	5.04	0.276	0.248	52.4%
2	5.47	Sequential	12.81	17.11	10.03	0.120	0.371	11.4%
3	28.8	Mixed	11.12	8.74	0.973	0.039	0.398	38.9%
4	28.8	Mixed	11.99	8.75	0.974	0.038	0.374	37.9%
5	28.8	Mixed	13.02	8.69	0.967	0.055	0.367	55.2%
6	28.8	Mixed	7.91	8.70	0.968	0.024	0.435	23.7%
7	28.8	Mixed	11.22	8.76	0.975	0.029	0.309	28.4%
8	28.8	Mixed	12.07	8.68	0.966	0.028	0.311	27.7%
9	28.8	Mixed	13.22	8.72	0.971	0.026	0.321	25.6%
lup	25.2	Mixed	12.97	8.77	1.12	0.031	0.249	26.5%
0	25.2	Mixed	12.98	9.08	1.16	0.066	0.393	54.5%
lup	25.2	Mixed	13.00	9.10	1.16	0.074	0.409	61.0%
1	25.2	Mixed	13.02	9.10	1.16	0.02	0.261	16.5%
lup	25.2	Mixed	12.99	9.12	1.16	0.017	0.376	14.0%
2	16.0	Mixed	12.99	5.80	1.16	0.070	0.246	57.7%
3	16.0	Mixed	13.05	5.79	1.16	0.013	0.189	10.7%
4	16.0	Mixed	12.55	5.78	1.16	0.031	0.234	25.6%
5	16.0	Mixed	12.49	5.80	1.16	0.013	0.144	10.7%
6	16.0	Mixed	12.01	5.85	1.17	0.016	0.259	13.1%
7	16.0	Mixed	12.05	5.82	1.16	0.011	0.080	9.0%
8	16.0	Mixed	10.50	0.601	0.120	0.00077	0.028	6.1%
9	16.0	Mixed	10.97	0.595	0.119	0.00023	0.021	1.8%
0	16.0	Mixed	10.50	0.614	0.123	0.00012	0.019	0.9%
2	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%

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[00134] Table VIII shows that the amount of PAA generated was independent of the method of introducing the triacetin and hydrogen peroxide to the buffer solutions. It can be seen that the pH of the buffer had a significant effect on the percent of the triacetin that was converted into PAA. Only when the pH was above 12 was a meaningful percent of the triacetin converted into PAA.

[00135] Example 9

[00136] A mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (63.4%) and triacetin (36.6%). Thus, the mole ratio of hydrogen peroxide:triacetin was 5.57:1. The mixture (13.68 g) was added to soft water such that the final solution contained 5 g/L of triacetin and had a pH of 4.1. Then, in successive experiments, sufficient 50% NaOH was added to the beaker so that the mole ratio of NaOH:TA was varied from 3:1 (obtained by introducing 5.49 g of 50% NaOH) to 8:1 (obtained by introducing 14.68 g of 50% NaOH). Using the ceric sulfate–iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the 6:1 mole ratio of NaOH:TA are shown in Table IX.

[00137] Table IX

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
0	0.015	0.437	2.9
1	0.275	0.298	53.1
3	0.312	0.274	60.2
5	0.326	0.258	62.9
11	0.302	0.233	58.3
21	0.246	0.199	47.5

[00138] It can be seen that even before the introduction of 50% NaOH, some PAA was present in solution as a result of being generated in the diluted mixture of the two components.

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Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.326% occurring at five minutes, corresponding to a yield of 62.9% assuming all three acetyl groups of triacetin were available for perhydrolysis.

[00139] This exercise was repeated for mole ratios of NaOH:triacetin ranging from 3:1 to 8:1. Table X summarizes the next set of data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

[00140] Table X

Mole ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.229	0.291	43.8	11.2
4:1	6	0.285	0.251	54.8	11.3
6:1	5	0.326	0.258	62.9	11.6
8:1	3	0.335	0.271	64.7	12.2

[00141] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.

[00142] Example 10

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[00143] A series of experiments was then performed in which the mole ratio of NaOH:TA was fixed at 8:1 and the mole ratio of hydrogen peroxide:triacetin was varied from 2:1 to 8:1. Triacetin (5 g) was added to about 965 mL of softened water along with 50.7% hydrogen peroxide in successive tests (3.06 g for the 2:1 mole ratio; 6.19 g for the 4:1 mole ratio; 9.23 g for the 6:1 mole ratio; and 12.32 g for the 8:1 mole ratio) to yield a solution with a pH of about 4.8-5.5. The volume of the mixture was adjusted to 990 mL with softened water. With mixing, 50% NaOH (14.67 g) was introduced. Using the ceric sulfate–iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the kinetic run employing the mole ratio of 8:6:1 NaOH:hydrogen peroxide:TA are shown in Table XI.

[00144] Table XI

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.331	0.317	63.8
3	0.330	0.303	63.6
5	0.319	0.303	61.5
10	0.300	0.295	57.8
20	0.256	0.274	49.3

[00145] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.331% occurring after just one minute, corresponding to a calculated conversion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for perhydrolysis.

[00146] This exercise was repeated for mole ratios of hydrogen peroxide:triacetin ranging from 2:1 to 6:1. Table XII summarizes the data and shows the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA

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generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

[00147] Table XII

Mole Ratio Hydrogen Peroxide:Triacetin	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
2:1	3	0.214	0.079	40.9	12.6
4:1	1	0.272	0.195	51.9	12.4
6:1	1	0.331	0.317	63.8	12.3
8:1	3	0.374	0.445	72.0	11.9

[00148] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between one and three minutes. The optimum mole ratio of hydrogen peroxide:triacetin was 8:1 as it resulted in the most efficient utilization of triacetin converted into PAA.

[00149] Example 11

[00150] A further series of experiments was performed in which the mole ratio of hydrogen peroxide to triacetin was fixed at 4:1 and the molar ratio of NaOH to triacetin was varied from 3:1 to 8:1. Triacetin (5 g) was added to around 975 mL of softened water along with 50.7% hydrogen peroxide (6.18 g) to yield a solution with a pH of 4.8 to 5.3. With mixing, 50% NaOH was introduced in successive tests (5.51 g for the 3:1 mole ratio; 7.30 g for the 4:1 mole ratio; 11.03 g for the 6:1 mole ratio; and 14.67 g for the 8:1 mole ratio). The volume of the mixture was adjusted to 1000 mL with softened water. Using the ceric sulfate–iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each

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sample point. The averages of the results for the kinetic run employing the mole ratio of NaOH:hydrogen peroxide:triacetin of 4:4:1 are shown in Table XIII.

[00151] Table XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.247	0.207	47.3
3	0.280	0.178	53.6
5	0.292	0.167	55.9
10	0.267	0.142	51.1
20	0.229	0.111	43.8

[00152] Upon addition of the NaOH, PAA was immediately generated, with the maximum amount of 0.292% occurring after five minutes, corresponding, to a calculated conversion of 55.9% triacetin into PAA assuming that all three acetyl groups of triacetin were available for perhydrolysis.

[00153] This exercise was repeated for mole ratios of NaOH:TA ranging from 3:1 to 8:1. Table XIV summarizes the data and records the maximum percent of PAA generated, the time after the addition of NaOH that it took to reach the maximum percent of PAA generated, the pH after the addition of the NaOH, the percent of hydrogen peroxide remaining at the time of the maximum percent of PAA, and the calculated percent of triacetin converted to PAA assuming that all three acetyl groups were available for perhydrolysis.

[00154] Table XIV

Mole Ratio NaOH:TA	Time at Max. PAA (min)	Max % PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)	pH
3:1	3	0.246	0.202	47.2	11.3
4:1	5	0.292	0.167	55.9	11.6
6:1	3	0.290	0.181	55.6	12.2
8:1	3	0.272	0.195	51.9	12.4

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[00155] It can be seen that the amount of PAA generated maximized when the mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1. The optimum mole ratio of NaOH:hydrogen peroxide:triacetin was 4:4:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 4:6:1 mole ratio of NaOH:hydrogen peroxide:triacetin. For all four mole ratios employed, the maximum amount of PAA was generated between three and five minutes.

[00156] Example 12

[00157] In the first test, a mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (54.24%) and triacetin (45.76%). Thus, the mole ratio of hydrogen peroxide:triacetin was 3.65:1. The mixture (51.22 g) was dissolved in soft water (911.9 g) in a one-liter beaker to yield a solution with a pH of 6.47. Then, 50% NaOH (36.47 g) was introduced with stirring. Thus, the mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin was 4.2:3.8:1. The pH of the resulting solution initially measured 12.1. Using the ceric sulfate–iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes. It was noticed that the sample temperature rose immediately upon addition of the 50% NaOH.

[00158] In the second test, the first test was repeated, except that the water was chilled soft water.

[00159] In the third test, the first test was repeated using three times the original amount of hydrogen peroxide:triacetin mixture and three times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (153.96 g) was introduced to chilled soft water (735.6 g) in a one-liter beaker to yield a solution with an initial pH of 5.14.

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Then, 50% NaOH (111.21 g) was introduced. Using the ceric sulfate–iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.

[00160] In the fourth test, the first test was repeated using four times the original amount of hydrogen peroxide:triacetin mixture and four times the original amount of 50% NaOH. The mole ratio of the combined mixture of NaOH:hydrogen peroxide:triacetin remained the same as before, at 4.2:3.8:1. The hydrogen peroxide and triacetin mixture (204.7 g) was introduced to chilled soft water (647.5 g) in a one-liter beaker to yield a solution with an initial pH of 6.32. Then, 50% NaOH (155.4 g) was introduced. Using the ceric sulfate–iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured over the next 10 minutes.

[00161] Table XV summarizes the results obtained for the four tests and shows the initial and final solution temperatures, the pH of the solution after the addition of the 50% NaOH, the maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

[00162] Table XV

Test #	Initial Temp. (°F)	Final Temp. (°F)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

[00163] Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA

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(assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

[00164] Table XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

[00165] The data in Tables XV and XVI indicate that far higher amounts of PAA are possible if the 50% sodium hydroxide solution is the last component of the mixture to be introduced. Further, up to 7.1% PAA was generated, although this solution got hot despite chilling the source water. Generation of the 6.3% PAA solution was very efficient because it represented a high 85.7% utilization of triacetin converted into PAA. There was clearly a linear relationship between Test 2, which generated 2.1% PAA, and Test 3, which utilized three times more of the reactants and generated 6.3% PAA. The data in Table XV indicate that the time of maximum conversion of triacetin was between one and four minutes. Thereafter, the amount of PAA in solution is reduced because it undergoes high pH degradation slowly over the following 10 minutes.

[00166] Example 13

[00167] Fig. 1 is a schematic representation of an example of a system 10 that was used to perform an embodiment of one of the methods described above to prepare a non-equilibrium solution of PAA on a site having a point-of-use. Triacetin was used as the acetyl precursor and 50% sodium hydroxide was used as the aqueous source of an alkali metal hydroxide.

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[00168] A container 120 of a hydrogen peroxide-acetyl precursor solution, which was a hydrogen peroxide-triacetin solution, and a container 140 of 50% sodium hydroxide were each equipped with chemical delivery diaphragm pumps 115 and 135, respectively. Inlet water 90, which was softened, was provided from a water source on the site having the point-of-use. Inlet water 90 was directed through a pressure regulator 100 and flow meter 105, then into a section of pipe where the hydrogen peroxide-triacetin solution was introduced through injection quill 110. Mixing was accomplished using static mixer 125. Then, the sodium hydroxide solution was added through injection quill 130 to form a reaction medium.

[00169] The hydrogen peroxide-triacetin solution and the sodium hydroxide solution may be added in a sequential manner as described, where the hydrogen peroxide-triacetin solution was added first, or they may be added to the water simultaneously through a "T" fitting placed before static mixer 125. If a T fitting is used, the hydrogen peroxide- triacetin solution and the 50% sodium hydroxide solution are introduced to opposite ends of the T fitting and the mixture is injected into the pipe of water. In other embodiments, the hydrogen peroxide and triacetin may be added separately, or sequentially, with either one first, or simultaneously, with the sodium hydroxide added either simultaneously with, or after, the hydrogen peroxide and triacetin.

[00170] The reaction medium was introduced to a residence chamber 145 which provided reaction time and contained a packing material to promote mixing. Residence chamber 145 was designed to be of a volume such that at a total flow rate of one gallon per minute, by the time the reaction medium reached sampling port 160, 30 seconds had elapsed since the sodium hydroxide solution had been added. A pH probe 155 monitored the pH of the mixture.

[00171] A controller 150 was interfaced to the flow meter 105 of the inlet water 90, and also to the chemical delivery diaphragm pumps 115 and 135. The controller 150 monitored the

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rate of the inlet water 90 and governed the rate at which the hydrogen peroxide-triacetin solution and the NaOH solution were introduced. If the flow of inlet water 90 decreased because of lower PAA requirements at the point-of-use 195, the rates at which the hydrogen peroxide-triacetin solution and the NaOH solution were pumped decreased accordingly. If the flow of inlet water 90 increased because of higher PAA requirements at the point-of-use 195, the rates at which the hydrogen peroxide-triacetin solution and the NaOH solution were pumped increased accordingly. If the flow of inlet water 90 stopped, pumps 115 and 135 stopped. Thus, the generation of PAA was both continuous and intermittent, and was tailored to the PAA requirements at the point-of-use.

[00172] The rate of the reaction between the hydrogen peroxide and the triacetin to form PAA is dependent upon the temperature of inlet water 90. If the temperature of inlet water 90 is high (for example, about 70°F), the maximum conversion of triacetin into PAA may occur after 30 seconds, in which case the entire reaction medium was directed to the point-of-use 195. However, if the temperature of inlet water 90 is low (for example, about 32°F), longer reaction times may be necessary to maximize the conversion of triacetin into PAA. Then, the reaction medium was directed through one or more residence chambers 165, 175, and 185 which also contained a packing material to promote turbulence and cause thorough mixing. Residence chambers 165, 175, and 185 were designed to be of volumes such that at a total flow rate of one gallon per minute, the reaction medium reached sampling port 170 in one minute, sampling port 180 in two minutes, and sampling port 190 in five minutes, to permit sampling at different time intervals.

[00173] Thus, depending on the temperature of the inlet water, the time to achieve the maximum conversion of hydrogen peroxide and triacetin into PAA was determined by sampling and analyzing the solution at sample ports 160, 170, 180, and 190. The entire flow was then

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directed from the sampling port with the highest amount of PAA to the point-of-use 195. In practice, the PAA generated from the reaction of hydrogen peroxide with triacetin is typically diluted at the point-of-use 195.

[00174] Point-of-use 195 may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products; fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

[00175] Example 14

[00176] Referring again to Fig. 1, a 55-gallon drum container 120 of a hydrogen peroxide-triacetin solution was prepared by mixing triacetin (251.5 lbs) with 50% hydrogen peroxide (298.4 lbs). The resulting 550 lbs of hydrogen peroxide-triacetin solution had a specific gravity of 1.19 g/mL (10 lbs/gal) and contained 54.3% hydrogen peroxide and 45.7% triacetin. Thus, the mole ratio of hydrogen peroxide:triacetin was 3.8:1. The apparatus depicted in Fig. 1 was used to continuously and intermittently prepare an approximately 1% PAA solution.

[00177] Softened local city water was directed through pressure regulator 100 at a flow rate of one gallon per minute as measured by flow meter 105. The container 120 of hydrogen peroxide-triacetin solution was equipped with a draw down tube so that the flow rate of the mixture could be measured. Diaphragm pump 115 injected the hydrogen peroxide-triacetin solution through injection quill 110. The hydrogen peroxide-triacetin solution was then mixed with the softened water using static mixer 125. A container 140 of 50% NaOH was also equipped with a draw down tube to measure the flow pumped by diaphragm pump 135 into injection quill 130.

[00178] The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate–iodometric

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titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

[00179] Table XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide-Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	~13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37
4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

[00180] It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing flow rate of NaOH. For this mole ratio of hydrogen peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

[00181] Example 15

[00182] *E. coli* O157:H7 bacteria (ATCC 35150) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one-liter test solutions.

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[00183] *Salmonella* typhimurium bacteria (ATCC 14028) was cultured in nutrient broth (Sigma, St. Louis, MO) by incubation for two days at 35°C. The bacteria were separated from the nutrient broth by centrifugation and carefully resuspended in two liters of sterile phosphate buffer, which was then split into two one-liter test solutions.

[00184] The amount of *E. coli* O157:H7 and *Salmonella typhimurium* bacteria were measured by serial dilution and plating on 3M *E. coli* plates and 3M *Enterobacteriaceae* Petrifilms, respectively.

[00185] A 1000 ppm stock of PAA was made by weighing 0.6386 g of Perasan MP-2 (5.83% hydrogen peroxide and 15.66% PAA) and adding water up to 100 g. Perasan MP-2 is an equilibrium product of PAA (Enviro Tech Chemical Services, Inc., Modesto, California). Side-by-side, one of the *E. coli* and one of the *Salmonella* test solutions were treated with a nominal dose of 1.0 ppm PAA by adding one mL of the 1000 ppm PAA stock solution to each sample. After one minute, approximately 100 mL of each test solution was removed, and sodium thiosulfate (0.5 g) was added to neutralize the PAA and hydrogen peroxide oxidants. After five minutes, sodium thiosulfate (0.5 g) was added to the remaining test solution to neutralize the PAA and hydrogen peroxide in the rest of the test solutions. The amount of viable *E. coli* O157:H7 and *Salmonella typhimurium* bacteria remaining in the test solutions at the one-minute and five-minute contact times were measured by serial dilution and plating on 3M *E. coli* Petrifilms and 3M *Enterobacteriaceae* Petrifilms, respectively.

[00186] A 1% solution of PAA was prepared by combining 30.90 g of a mixture of 50% hydrogen peroxide and triacetin (54.22% hydrogen peroxide and 45.78% triacetin) with 929.4 g of water, and then adding 50% NaOH (40.53 g). The PAA solution had a pH of 12.79. The mole ratio of this mixture was 3.8:7.8:1 NaOH:hydrogen peroxide:triacetin. One minute after preparation, the second one-liter *E. coli* solution and the second one-liter *Salmonella* solution

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were treated with a nominal dose of 1.0 ppm PAA by adding 0.10 g of the 1% PAA solution to each sample. The test solution contact times, neutralization, and plating procedures were replicated for those that employed PAA from Perasan MP-2.

[00187] All 3M *E. coli* Pertrifilms and 3M *Enterobacteriaceae* Petrifilms were incubated at 35°C for 24 hours. After incubation, the plates were enumerated.

[00188] Table XVIII shows the microbiological results of the *E. coli* O157:H7 test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. The *E. coli* test solution started with $\log_{10}$ 6.99 CFU/mL prior to being treated with 1.0 ppm of PAA from Perasan MP-2 or with 1 ppm of PAA from the 1% PAA solution.

[00189] The *E. coli* test solution treated with 1.0 ppm PAA from Perasan MP-2 contained a $\log_{10}$ 6.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, $\log_{10}$ 6.34 CFU/mL remained (77.50% reduction). The *E. coli* solution treated with a nominal 1.0 ppm PAA from the 1% PAA solution contained a $\log_{10}$ 6.78 CFU/mL after one minute and 6.63 CFU/mL after five minutes, respectively, corresponding to 38.02% and 56.12% reductions, respectively.

[00190] Table XVIII

***E. coli* O157:H7**

Description	$\log_{10}$ CFU/ml remaining	$\log_{10}$ reduction	% reduction
Control	6.99	N/A	N/A
Perasan MP-2 (1 min)	6.74	0.25	43.48
Perasan MP-2 (5 min)	6.34	0.65	77.50
1% PAA solution (1 min)	6.78	0.21	38.02
1% PAA solution (5 min)	6.63	0.36	56.12

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[00191] Table XIX shows the microbiological results of the *Salmonella typhimurium* test solutions before treatment with PAA, one minute after the samples were dosed with a nominal 1.0 ppm PAA, and five minutes after being dosed with PAA. The *Salmonella* test solution started with $\log_{10}$ 7.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.

[00192] The *Salmonella* solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a $\log_{10}$ 1.76 CFU/mL after one minute and 0.70 CFU/mL after five minutes, corresponding to >99.999% reduction at both contact times. The *Salmonella* test solution treated with 1.0 ppm PAA from the 1% PAA solution contained a $\log_{10}$ 6.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, $\log_{10}$ 4.95 CFU/mL remained (99.24% reduction).

[00193] Table XIX

Salmonella typhimurium			
Description	$\log_{10}$ CFU/ml remaining	$\log_{10}$ reduction	% reduction
Control	7.07	N/A	N/A
Perasan MP-2 (1 min)	1.76	5.31	99.9995
Perasan MP-2 (5 min)	0.70	6.37	>99.9999
1% PAA solution (1 min)	6.69	0.38	58.31
1% PAA solution (5 min)	4.95	2.12	99.24

[00194] The data in tables XVIII and XIX demonstrate that the 1% PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%, about equal to that of the Perasan MP-2, which was > 99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

[00195] **5. Solid Compositions for Bleaching and Stain Removal**

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[00196] A freely-flowable, solid peroxygen bleaching and stain removal composition comprises a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity. A preferable liquid acetyl precursor is triacetin. The water soluble solid source of hydrogen peroxide is preferably sodium percarbonate, although sodium perborate monohydrate or sodium perborate tetrahydrate may be used. The water-soluble solid source of alkalinity acts as a pH control agent, and may be an alkali metal or earth alkali metal bicarbonate, carbonate, sesquicarbonate, borate, silicate, or hydroxide. Examples include sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, sodium borate, sodium borate decahydrate (borax), sodium metasilicate, and sodium hydroxide.

[00197] In an embodiment, the composition comprises about 0.99% to about 8.45% triacetin, about 13% to about 54% sodium percarbonate, and about 24% to about 44% solid source of alkalinity.

[00198] The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispercency, and lower surface tension.

[00199] Metal ions present in the bleaching medium can have a tendency to deposit on the substrates being bleached. Therefore, the solid bleaching composition may optionally contain a metal chelating agent such as a polyacrylate, a phosphonate, a maleic acid, a salt of ethylenediaminetetraacetic acid, a salt of nitrilotriacetic acid, or a salt of gluconic acid.

[00200] Surfactants reduce the surface tension of the bleaching medium and enhance the process of cleaning the soiled article. Surfactants also disperse the soil particles removed from the article and keep them suspended. Therefore, the solid bleaching composition may optionally contain a surfactant, such as an anionic, cationic, amphoteric, or non-ionic surfactant.

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[00201] The solid bleaching composition may also optionally contain a solid zeolite, such as sodium zeolite, which acts to capture calcium and magnesium ions that may be present in the bleaching medium that would otherwise interact with an anionic surfactant, causing the surfactant to precipitate and removing it from the bleaching medium.

[00202] The composition may also optionally contain an inert, solid filler, such as anhydrous sodium sulfate, sodium sulfate decahydrate, or sodium chloride. The filler increases the total ionic strength of the aqueous phase, but imparts no chemical properties to the bleaching medium.

[00203] To make the solid peroxygen bleaching and stain removal composition, the water soluble solid source of hydrogen peroxide, the water-soluble solid source of alkalinity, any chelating agent, any sufactant, and any filler are blended with the liquid triacetin to form a solid bleaching composition. The components may be added in any order. Any blending equipment may be used. Suitable examples of equipment include a ribbon and paddle blender, a V and double-cone blender, a Nauta screw mixer, and a rotating cement mixer. Alternatively, the ingredients may be blended by milling using a pulveriser mill, a ball mill, a hammer mill, a pin mill, an air mill, or a roller mill. Blending is performed for sufficient time to create a homongenous mixture. The mixture is a freely-flowable solid which is readily discharged from the blender.

[00204] Example 16

[00205] A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non-flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.

[00206] Table XX

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Component	%
Sodium carbonate, anhydrous	26.3
Sodium percarbonate	58.9
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

[00207] This solid peroxygen bleach precursor was then blended with incrementally increasing amounts of liquid triacetin. At each addition, the product was examined for flowability and for the odor of PAA. Table XXI summarizes the findings when up to 9.1g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

[00208] Table XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely- flowable solid	None
2	Freely- flowable solid	None
3	Freely- flowable solid	None
4	Freely- flowable solid	None
5	Freely- flowable solid	None
6	Freely- flowable solid	None
7	Freely- flowable solid	None
8	Freely- flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

[00209] Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45g of the triacetin to form a freely-flowable solid composition, without becoming a sticky, non-flowable product which would not pour easily or would become a solid mass upon storage inside a container.

[00210] The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.

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[00211] Table XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

[00212] Another unexpected result was that after storing the composition for over one year at ambient temperature, the composition still had not developed an odor of PAA.

[00213] These surprising results are in contrast to the current belief that a liquid acetyl precursor, such as triacetin, could not be utilized with a solid source of hydrogen peroxide in a non-chlorine peroxygen bleaching and stain removal composition, for at least two reasons. First, when a non-chlorine peroxygen bleaching composition is used in residential and commercial laundering applications, the product must be a freely-flowable solid. Typically, the acetyl precursor in a non-chlorinated peroxygen bleach is present in amounts up to 10%. It was believed that blending a liquid at this level with the other dry components of the laundry bleach would create a sticky, clumping mass, rather than a freely-flowable solid, and would therefore not be acceptable to the user. Second, it was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

[00214] Example 17

[00215] Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.

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[00216] Table XXIII

Components of Composition A	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	41	615
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	4	60
Soda Ash	16	240

Components of Composition B	%	Charge Weights, g
Premix 1		
Sodium Percarbonate	13	195
NANSA HS 90	1.5	22.5
Sodium Metasilicate (Anhydrous)	19.5	292.5
Sodium Sulfate (Anhydrous)	43	645
Triacetin	4	60
Premix 2		
Mineral Oil	1	15
Sodium Hydroxide Beads	2	30
Soda Ash	16	240

[00217] In both cases, Premix 1 was prepared by kneading the NANSA HS 90 (a sodium dodecylbenzenesulfonate surfactant) with the sodium sulfate. The sodium sulfate helped break up the sticky surfactant efficiently. Then, the sodium percarbonate, the sodium metasilicate, and the triacetin were added and mixed by hand.

[00218] In both cases, Premix 2 was prepared by mixing the sodium hydroxide beads with the mineral oil to afford a well-coated mixture, with some free-standing mineral oil remaining. Soda ash was blended in portions to take up the excess liquid and to provide a free-flowing solid mixture.

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[00219] Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

[00220] Both compositions A and B, which were held in uncovered bowls at ambient temperature after preparation, exhibited slow weight gain over time, most likely due to absorbance of water from the air. Each composition had gained 2.4% of its initial weight over a period of three days.

[00221] Neither composition exhibited significant exothermic behavior. However, composition A was hotter at the end of preparation and cooled more slowly than composition B. The temperature of composition A was 85°F immediately after preparation, rose to 88°F over the next ten minutes, and then fell slowly to 74°F. The temperature of composition B was 80°F immediately after preparation, rose to 81°F over the next twenty minutes, and then fell slowly to 65°F.

[00222] The solid peroxygen bleaching and stain removal composition described above may be used as follows.

[00223] First, the solid peroxygen, composition is introduced to an aqueous medium that is used for bleaching or stain removal of at least one article contained within the aqueous medium. For bleaching of laundry articles, about 5g of bleaching composition is introduced for every liter of water used in the bleaching cycle. For home use, the bleaching composition can be added manually at the start of the wash. For commercial laundry systems, the bleaching composition may be introduced just before the bleaching cycle, toward the end of the wash and following the soil removal cycle. In most commercial and residential laundry machines, bleaching cycles are typically about 10-15 minutes.

[00224] Second, the composition is allowed to dissolve and react to form the bleaching medium containing PAA. The solid source of hydrogen peroxide, such as sodium percarbonate,

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and the solid source of alkalinity, such as sodium hydroxide, dissolve in the laundry water and cause the pH of the water to increase to above about 10.5.

[00225] While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:

$$H_2O_2 = H^+ + HO_2^-$$

[00226] The perhydroxyl anion (HO_2^-) then effects nucleophilic substitution reactions on the carbonyl groups of triacetin, in a perhydrolysis reaction, to form PAA and 1,2,3-propanetriol (glycerine). The laundry water would also contain unreacted hydrogen peroxide, unreacted triacetin, and sodium hydroxide.

[00227] Third, the aqueous solution of PAA and the unreacted hydrogen peroxide are mixed for sufficient time to effect bleaching or stain removal of the articles contained within the aqueous medium. Both commercial and residential bleaching cycles are about 10-15 minutes.

[00228] Fourth, the article is rinsed with fresh water so that it becomes substantially free of PAA and the unreacted hydrogen peroxide, the glycerine, the unreacted triacetin, and the sodium hydroxide. Generally, for a laundered article, the washing machine is programmed to empty the bleaching medium and replace it with fresh water. The machine can agitate the articles with the rinse water to enhance the rinsing process.

[00229] Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

[00230] Example 18

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[00231] Laundry swatches were made by cutting a tea towel into 50 equal 5 x 4 inch sheets. They were then separated into seven groups of seven swatches. Six of the groups were stained and the seventh group was left unstained for comparison purposes. Five of the groups that were stained were stained by soaking them in one of the following: black tea, black coffee, red wine, blood (pork), and acetone-extracted chlorophyll. The sixth group of swatches was stained by rubbing them on green grass. After allowing the stained swatches to dry, and before challenging the stains, the swatches were set aside for two months to allow the stains to set in the fabric.

[00232] A solid peroxygen bleaching and stain removal composition (200 g) was prepared by blending sodium percarbonate (104.0 g), triacetin (8.00 g), soda ash (80.01 g), and sodium hydroxide beads (8.00 g). The final product was a freely-flowable solid.

[00233] The composition was tested using 1:100 dilution at both 75°F and 104°F. The initial pH was measured and the concentrations of PAA and hydrogen peroxide were evaluated using the method of U.S. patent no. 7,651,724. At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75°F, the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104°F had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H_2O_2). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75°F at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104°F at a pH of 11.2.

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[00234] Table XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

[00235] Table XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426
5.5	133	1494
7.8	122	1427
10.3	119	1405

[00236] The stain removal ability of the composition was determined by comparing treated swatches to control swatches (swatches washed in just city water for the same amount of time and at elevated temperature) and non-stained swatches. The description of the swatches is set forth in Table XXVI. Three stained swatches were used for each test. The composition (10.0 g) was weighed into a beaker (2000 mL). To this beaker a measured amount of hard water (990.0 g) was added at ambient temperature (64°F). The swatches were added to the solution and agitated by mixing with a plastic utensil for 10 minutes to simulate a laundry bleaching cycle. After 10 minutes, the wash water was discarded and a water rinse was performed by adding fresh city water (1000.0 g) to the swatches and agitating for two minutes using the same plastic utensil. The swatches were immediately removed from the beaker after rinsing, wrung out by hand, and laid to dry. These steps were then repeated using water at an elevated temperature (120°F).

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[00237] A control swatch was obtained by taking one swatch at a time from each stain group and washing in city water at an elevated temperature (120°F) for 10 minutes in the same manner as the treated swatches. After the wash, the swatches were immediately removed, wrung out by hand, and laid to dry.

[00238] Table XXVI

Type of Swatches	Description
Treated Swatches	Swatches subjected to bleaching for 10 minutes using bleaching formulation with triacetin and a 2-minute rinse with hard water
Control Swatches	Swatches subjected to only an elevated temperature (120°F) hard water wash for 10 minutes
Non-Stained Swatches	Non-altered swatches

[00239] The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

[00240] Table XXVII

Type of Stain	Bleaching Formula at 64°F	Bleaching Formula at 120°F
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

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[00241] It can be seen that, in general, the composition displayed enhanced stain removal properties at elevated temperature. Excellent stain removal properties were obtained for black tea and black coffee, and more moderate performance with red wine and blood. The composition had virtually no effect on grass stains or the chlorophyll pigment that was acetone-extracted from green grass.

[00242] The invention has been described above with the reference to the preferred embodiments. Those skilled in the art may envision other embodiments and variations of the invention that fall within the scope of the claims.

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Designation of inventor

User reference: AT-BF-G49415
Application No:

	Inventor	
	Name:	HOWARTH Jonathan . N.
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	The applicant has acquired the right to the European patent:	As employer

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Designation of inventor

User reference: AT-BF-G49415
Application No:

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	The applicant has acquired the right to the European patent:	As employer

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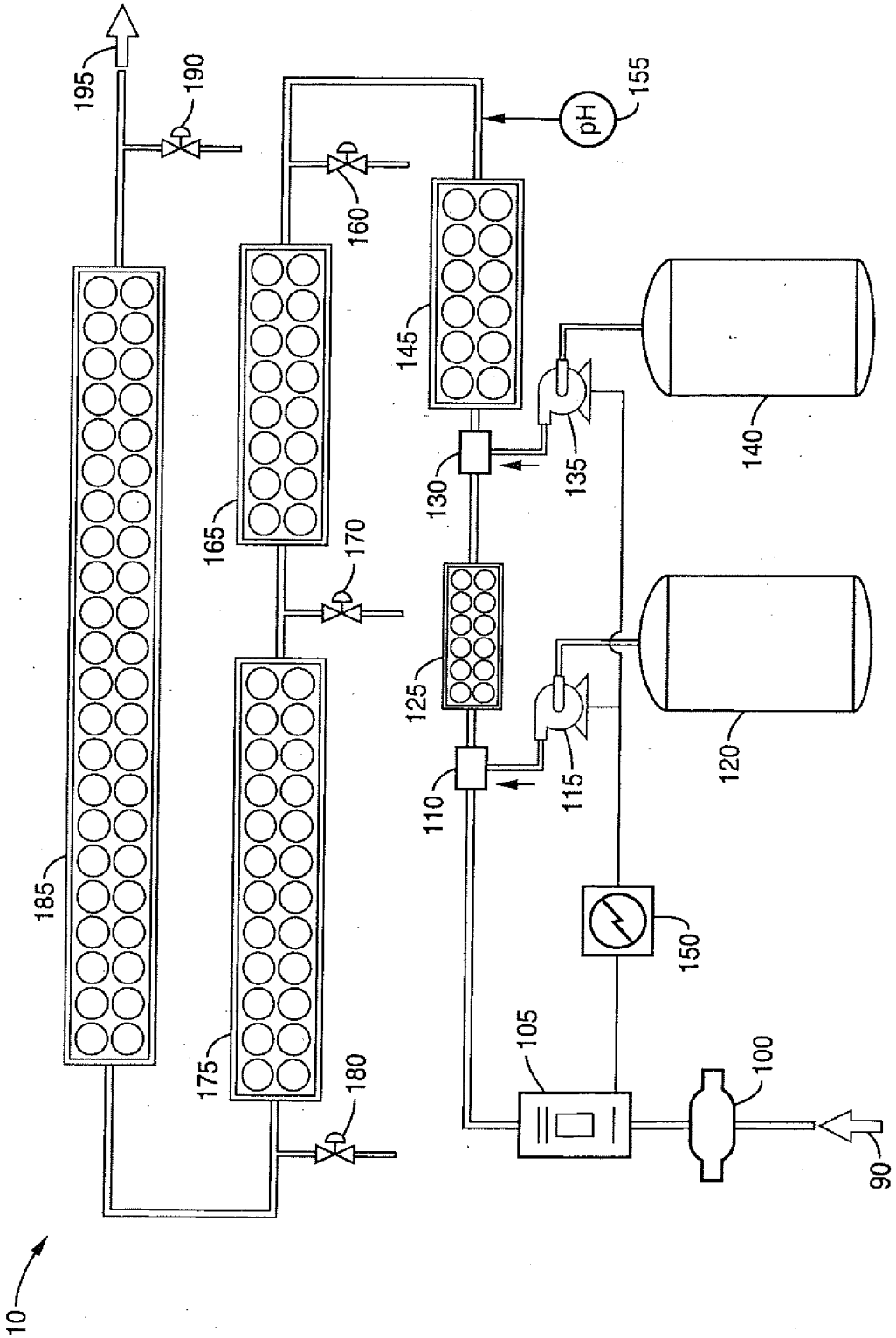

195
190
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pH
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145
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165
170
125
120
115
110
185
150
105
100
175
180
90
10

FIG. 1

Europäisches Patentamt
European Patent Office
Office européen des brevets

Request for grant of a European patent

For official use only		
1 Application number:	MKEY	**MKEY - EP14185786.2**
2 Date of receipt (Rule 35(2) EPC):	DREC	**DREC - 22 Sep 2014**
3 Date of receipt at EPO (Rule 35(4) EPC):	RENA	
4 Date of filing:		

5 Grant of European patent, and examination of the application under Article 94, are hereby requested. ☒

5.1 The applicant waives his right to be asked whether he wishes to proceed further with the application (Rule 70(2)) ☐

Procedural language: en

Description and/or claims filed in: en

6 Applicant's or representative's reference: AT-BF-G49415

Applicant 1

7-1 Name: Enviro Tech Chemical Services Inc

8-1 Address:
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United States of America

10-1 State of residence or of principal place of business: United States of America

14.1 The/Each applicant hereby declares that he is an entity or a natural person under Rule 6(4) EPC. ☐

Representative 1

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Inventor(s)

23 Inventor details filed separately ☒

24 **Title of invention**

Title of invention: Methods and Compositions for the generation of peracetic acid on site at the point-of-use.

25 **Declaration of priority (Rule 52)**

A declaration of priority is hereby made for the following applications

25.2 This application is a complete translation of the previous application ☐

25.3 It is not intended to file a (further) declaration of priority ☐

26 **Reference to a previously filed application**

27 **Divisional application** ☒

Application number of earlier application: EP11861339.7

Date of Filing (Art. 80/Rule 40 EPC): 24 March 2011

27.1 This divisional application is of the following generation: ☒ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 or subsequent

28 **Article 61(1)(b) application** ☐

29 **Claims**

Number of claims: 14

29.1 ☒ as attached

29.2 ☐ as in the previously filed application (see Section 26.2)

29.3 ☐ The claims will be filed later

30 **Figures**

It is proposed that the abstract be published together with figure No. 1

31 **Designation of contracting states**

All the contracting states party to the EPC and valid for the parent application at the time of filing of this divisional application are deemed to be designated (see Article 76(2)).

32 **Different applicants for different contracting states**

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33 Extension/Validation

This application is deemed to be a request to extend the effects of the European patent application and the European patent granted in respect of it to all non-contracting states to the EPC with which extension or validation agreements are in force on the date on which the application is filed. However, the request is deemed withdrawn if the extension fee or the validation fee, whichever is applicable, is not paid within the prescribed time limit.

33.1 It is intended to pay the extension fee(s) for the following state(s):

33.2 It is intended to pay the validation fee(s) for the following state(s): Not applicable

34 Biological material

38 Nucleotide and amino acid sequences

The European patent application contains a sequence listing as part of the description ☐

The sequence listing is attached in computer-readable format in accordance with WIPO Standard ST.25 ☐

The sequence listing is attached in PDF format ☐

Further indications

39 Additional copies of the documents cited in the European search report are requested

Number of additional sets of copies:

40 Refund of the search fee under to Article 9 of the Rules relating to Fees is requested ☐

Application or publication number of earlier search report:

42 Payment

Mode of payment: Debit from deposit account

The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees section below.

Currency: EUR

Deposit account number: 28050202

Account holder: Bailey Walsh & Co LLP

Deferred execution date / total amount to be debited on: (or on the date of receipt if the submission date is after the deferred execution date you have indicated)

Important information:
• This functionality allows you to indicate explicitly that your payment order is to be executed at a later date than the submission date. In this case, the payment date will be deemed to be the deferred execution date, provided that you have sufficient funds on your deposit account on that date.
• Please choose the deferred execution date option only if the fees are to be debited on a future date, as otherwise the default execution date is date of receipt.
• The deferred execution date can be a maximum of 40 days in the future.

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43 Refunds

Any refunds should be made to EPO deposit account:	28050202
Account holder:	Bailey Walsh & Co LLP

Fees	Factor applied	Fee schedule	Amount to be paid
001 Filing fee - EP direct - online	1	120.00	120.00
002 Fee for a European search - Applications filed on/after 01.07.2005	1	1 285.00	1 285.00
005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009	1	580.00	580.00
006 Examination fee - For applications filed on/after 01.07.2005	1	1 620.00	1 620.00
015 Claims fee - For the 16th to the 50th claim	0	235.00	0.00
015e Claims fee - For the 51st and each subsequent claim	0	580.00	0.00
033 Renewal fee for the 3rd year	1	465.00	465.00
034 Renewal fee for the 4th year	1	580.00	580.00
501 Additional filing fee for the 36th and each subsequent page	29	15.00	435.00
Total:		EUR	5 085.00

44-A Forms		Details:	System file name:
A-1	Request		as ep-request.pdf
A-2	1. Designation of inventor	1. Inventor	as F1002-1.pdf
A-3	2. Designation of inventor	2. Inventor	as F1002-2.pdf

44-B Technical documents		Original file name:	System file name:
B-1	Specification	X11031-EP Abstract.pdf abstract	SPECEPO-2.pdf
B-2	Specification	X11031-EP Figures.pdf 1 figure(s)	SPECEPO-3.pdf
B-3	Specification	G49415-claims clean.pdf 14 claims	SPECEPO-4.pdf
B-4	Specification	X11031-EP Spec 01.pdf Description	SPECEPO-1.pdf

44-C Other documents	Original file name:	System file name:

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General authorisation:

46 Signature(s)

Place:	Leeds, UK
Date:	22 September 2014
Signed by:	Alexandra Tomkinson 4603
Association No.:	Bailey Walsh & Co LLP
Capacity:	(Representative)

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