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***December 11, 2024***

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UNITED STATES PATENT AND TRADEMARK OFFICE · DEPARTMENT OF COMMERCE

**Certified by**

Katherine Kelly Vidal

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PTO/SB/05 (08-08)
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# UTILITY PATENT APPLICATION TRANSMITTAL

*(Only for new nonprovisional applications under 37 CFR 1.53(b))*

| | | |
|---|---|---|
| *Attorney Docket No.* | 8568/17669 | U.S. PTO 13/065553 |
| *First Inventor* | Michael S. Harvey | 03/24/2011 |
| *Title* | Methods...Peracetic Acid...Use | |
| *Express Mail Label No.* | EV 419585747US | |

## APPLICATION ELEMENTS

*See MPEP chapter 600 concerning utility patent application contents.*

1. ☑ **Fee Transmittal Form** (e.g., PTO/SB/17)
2. ☑ **Applicant claims small entity status.** See 37 CFR 1.27.
3. ☑ **Specification** [*Total Pages* 74 ]
   Both the claims and abstract must start on a new page
   *(For information on the preferred arrangement, see MPEP 608.01(a))*
4. ☑ **Drawing(s)** (*35 U.S.C. 113*) [*Total Sheets* 1 ]
5. **Oath or Declaration** [*Total Sheets* 7 ]
   a. ☑ Newly executed (original or copy)
   b. ☐ A copy from a prior application (37 CFR 1.63(d))
   *(for continuation/divisional with Box 18 completed)*
   i. ☐ DELETION OF INVENTOR(S)
   Signed statement attached deleting inventor(s) name in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
6. ☐ **Application Data Sheet.** See 37 CFR 1.76
7. ☐ **CD-ROM or CD-R** in duplicate, large table or Computer Program *(Appendix)*
   ☐ Landscape Table on CD
8. **Nucleotide and/or Amino Acid Sequence Submission**
   *(if applicable, items a. – c. are required)*
   a. ☐ Computer Readable Form (CRF)
   b. Specification Sequence Listing on:
      i. ☐ CD-ROM or CD-R (2 copies); or
      ii. ☐ Paper
   c. ☐ Statements verifying identity of above copies

*ADDRESS TO:* **Commissioner for Patents**
**P.O. Box 1450**
**Alexandria VA 22313-1450**

## ACCOMPANYING APPLICATION PARTS

9. ☐ **Assignment Papers** (cover sheet & document(s))
   Name of Assignee_____
10. ☐ **37 CFR 3.73(b) Statement** *(when there is an assignee)* ☑ **Power of Attorney** (combined)
11. ☐ **English Translation Document** *(if applicable)*
12. ☐ **Information Disclosure Statement** (PTO/SB/08 or PTO-1449)
    ☐ Copies of citations attached
13. ☐ **Preliminary Amendment**
14. ☑ **Return Receipt Postcard** (MPEP 503)
    *(Should be specifically itemized)*
15. ☐ **Certified Copy of Priority Document(s)**
    *(if foreign priority is claimed)*
16. ☐ **Nonpublication Request** under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent.
17. ☐ Other:_____

18. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below and in the first sentence of the specification following the title, or in an Application Data Sheet under 37 CFR 1.76:*

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: .....

*Prior application information:* *Examiner* _____ *Art Unit:* _____

## 19. CORRESPONDENCE ADDRESS

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| Signature | Audrey A. Millemann | Date | March 23, 2011 |
| Name (Print/Type) | Audrey A. Millemann | Registration No. (Attorney/Agent) | 44,942 |

This collection of information is required by 37 CFR 1.53(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
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*Effective on 12/08/2004.*
*Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).*

# FEE TRANSMITTAL
## For FY 2009

☑ Applicant claims small entity status. See 37 CFR 1.27

**TOTAL AMOUNT OF PAYMENT** ($) 3271

| Complete if Known | |
|---|---|
| Application Number | |
| Filing Date | |
| First Named Inventor | Michael S. Harvey |
| Examiner Name | |
| Art Unit | |
| Attorney Docket No. | 8568/17669 |

**METHOD OF PAYMENT** (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____

☑ Deposit Account Deposit Account Number: 501176 Deposit Account Name: Weitraub Genshlea Chediak

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☑ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, **except for the filing fee**

☑ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☑ Credit any overpayments

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**FEE CALCULATION**

**1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

| Application Type | FILING FEES Fee ($) | FILING FEES Small Entity Fee ($) | SEARCH FEES Fee ($) | SEARCH FEES Small Entity Fee ($) | EXAMINATION FEES Fee ($) | EXAMINATION FEES Small Entity Fee ($) | Fees Paid ($) |
|---|---|---|---|---|---|---|---|
| Utility | 330 | 165 | 540 | 270 | 220 | 110 | 545 |
| Design | 220 | 110 | 100 | 50 | 140 | 70 | |
| Plant | 220 | 110 | 330 | 165 | 170 | 85 | |
| Reissue | 330 | 165 | 540 | 270 | 650 | 325 | |
| Provisional | 220 | 110 | 0 | 0 | 0 | 0 | |

**2. EXCESS CLAIM FEES**

| Fee Description | Fee ($) | Small Entity Fee ($) |
|---|---|---|
| Each claim over 20 (including Reissues) | 52 | 26 |
| Each independent claim over 3 (including Reissues) | 220 | 110 |
| Multiple dependent claims | 390 | 195 |

| Total Claims | | Extra Claims | | Fee ($) | | Fee Paid ($) |
|---|---|---|---|---|---|---|
| 91 | - 20 or HP = | 71 | x | 26 | = | 1846 |

HP = highest number of total claims paid for, if greater than 20.

| Indep. Claims | | Extra Claims | | Fee ($) | | Fee Paid ($) |
|---|---|---|---|---|---|---|
| 12 | - 3 or HP = | 8 | x | 110 | = | 880 |

HP = highest number of independent claims paid for, if greater than 3.

| Multiple Dependent Claims Fee ($) | Fee Paid ($) |
|---|---|
| | |

**3. APPLICATION SIZE FEE**

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is $270 ($135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

| Total Sheets | | Extra Sheets | | Number of each additional 50 or fraction thereof | | Fee ($) | | Fee Paid ($) |
|---|---|---|---|---|---|---|---|---|
| 74 | - 100 = | 0 | / 50 = | | (round up to a whole number) x | | = | |

**4. OTHER FEE(S)**

| | Fees Paid ($) |
|---|---|
| Non-English Specification, $130 fee (no small entity discount) | |
| Other (e.g., late filing surcharge): | |

**SUBMITTED BY**

| | | | |
|---|---|---|---|
| Signature | Audrey A. Millemann | Registration No. (Attorney/Agent) 44,942 | Telephone 916-558-6033 |
| Name (Print/Type) | Audrey A. Millemann | | Date March 23, 2011 |

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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# METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE

Michael S. Harvey and Jonathan N. Howarth

## 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

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

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

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

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.

**[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

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.

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

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

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.

**[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**

**[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:

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

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

**[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

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. <u>Liquid Compositions for Generating Non-Equilibrium Solutions of PAA On a Site Having a Point-of-Use</u>**

**[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.

**[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

**[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

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

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

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 |

[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%.

[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

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

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.

[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.

**[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

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.

**[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.

**[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

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

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

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.

[00133] Table VIII

| Test # | 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 |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.99 | Double | 10.50 | 8.60 | 5.53 | 0.170 | 0.329 | 29.6% |
| 2 | 5.47 | Double | 10.50 | 8.60 | 5.04 | 0.178 | 0.333 | 33.9% |
| 3 | 5.45 | Double | 10.80 | 8.61 | 5.07 | 0.192 | 0.329 | 36.4% |
| 4 | 5.68 | Double | 11.00 | 8.87 | 5.01 | 0.201 | 0.322 | 38.6% |
| 5 | 5.72 | Double | 11.00 | 9.13 | 5.12 | 0.068 | 0.416 | 12.8% |
| 6 | 5.49 | Double | 12.42 | 8.60 | 5.02 | 0.169 | 0.306 | 32.4% |
| 7 | 5.59 | Double | 12.91 | 8.60 | 4.93 | 0.320 | 0.265 | 62.4% |
| 8 | 5.53 | Double | 12.80 | 8.69 | 5.04 | 0.335 | 0.273 | 63.9% |
| 9 | 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% |
| 19 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% |
| 20 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% |
| 21 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% |

**[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.

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

**[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

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

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 |

**[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.

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

(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.

**[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

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

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

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.

**[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

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 |

**[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**

**[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.

**[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

| 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.

[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.

[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.

**[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,

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

**[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.

[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).

**[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 |

**[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.

## Claims

We claim:

1. A hydrogen peroxide-acetyl precursor solution, comprising:

    a. aqueous hydrogen peroxide;

    b. a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide;

    c. a trace amount of peracetic acid; and

    d. water.

2. The solution of claim 1, wherein said liquid acetyl precursor is triacetin.

3. The solution of claim 2, wherein said aqueous hydrogen peroxide is about 23% to about 40% and said triacetin is about 20% to about 53%, and further wherein the mole ratio of said hydrogen peroxide to said triacetin is about 2.98:1 to about 12.84:1.

4. The solution of claim 3, wherein said aqueous hydrogen peroxide is about 27% and said triacetin is about 46%, and further wherein said mole ratio of said hydrogen peroxide to said triacetin is about 3.8:1.

5. A method of preparing a hydrogen peroxide-acetyl precursor solution, comprising:

    a. introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and

    b. allowing the liquid acetyl precursor and the solution of aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

6. The composition of claim 5, wherein the liquid acetyl precursor is triacetin.

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

a. providing water;

b. introducing a hydrogen peroxide-acetyl precursor solution to the water;

c. mixing the hydrogen peroxide-acetyl precursor solution and 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.

8. The method of claim 7, further comprising, prior to step (b), a step of providing the hydrogen peroxide-acetyl precursor solution comprising: introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the liquid acetyl precursor and the solution of aqueous hydrogen peroxide to mix to form the hydrogen peroxide-acetyl precursor solution.

9. The method of claim 8, wherein the liquid acetyl precursor is triacetin defining a hydrogen peroxide-triacetin solution.

10. The method of claim 9, wherein the hydrogen peroxide-triacetin solution has a mole ratio of hydrogen peroxide to triacetin of about 2.98:1 to about 12.84:1.

11. The method of claim 7, wherein the provided water is an aqueous stream.

12. The method of claim 7, wherein the provided water is contained in a mixing tank or other vessel.

13. The method of claim 9, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

14. The method of claim 13, wherein the sodium hydroxide is about 1.82% to about 7.28%.

15. The method of claim 7, wherein step (d) is performed simultaneously with step (b).

16. The method of claim 7, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

17. The method of claim 16, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

18. The method of claim 17, further comprising, after step (e), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

19. The method of claim 16, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

20. The method of claim 14, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

21. The method of claim 7, wherein steps (a) through (e) are performed on a continuous basis.

22. The method of claim 7, wherein steps (a) through (e) are performed on an intermittent basis.

23. The method of claim 7, wherein the peracetic acid solution is for immediate use.

24. The method of claim 7, further comprising, after step (e), a step of adding a source of acid to stabilize the non-equilibrium solution of peracetic acid for storing and using throughout a working day.

25. The method of claim 7, wherein the peracetic acid solution is prepared on a site having a point-of-use.

26. A method of generating a non-equilibrium solution of peracetic acid for use on a site having a point-of-use of peracetic acid, comprising:

a. providing water on a site;

b. providing a hydrogen peroxide-acetyl precursor solution on the site having a point-of-use;

c. introducing the hydrogen peroxide-acetyl precursor solution to the water;

d. mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture;

e. providing an aqueous source of an alkali metal or earth alkali metal hydroxide on the site having the point-of-use;

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

g. forming a reaction medium comprising a non-equilibrium solution of peracetic acid for use at the point-of-use of peracetic acid.

27. The method of claim 26, further comprising, prior to step (b), a step of providing the hydrogen peroxide-acetyl precursor solution comprising: introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the liquid acetyl precursor and the solution of aqueous hydrogen peroxide to mix to form the hydrogen peroxide-acetyl precursor solution.

28. The method of claim 8, wherein the liquid acetyl precursor is triacetin defining a hydrogen peroxide-triacetin solution.

29. The method of claim 28, wherein the hydrogen peroxide-triacetin solution has a mole ratio of hydrogen peroxide to triacetin of about 2.98:1 to about 12.84:1.

30. The method of claim 26, wherein the provided water is an aqueous stream.

31. The method of claim 26, wherein the provided water is contained in a mixing tank or other vessel.

32. The method of claim 28, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

33. The method of claim 32, wherein the sodium hydroxide is about 1.82% to about 7.28%.

34. The method of claim 26, wherein step (d) is performed simultaneously with step (b).

35. The method of claim 26, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

36. The method of claim 35, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

37. The method of claim 36, further comprising, after step (e), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

38. The method of claim 35, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

39. The method of claim 33, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

40. The method of claim 26, wherein steps (a) through (e) are performed on a continuous basis.

41. The method of claim 26, wherein steps (a) through (e) are performed on an intermittent basis.

42. The method of claim 26, wherein the peracetic acid solution is for immediate use.

43. The method of claim 26, further comprising, after step (e), a step of adding a source of acid to stabilize the non-equilibrium solution of peracetic acid for storing and using throughout a working day.

44. The method of claim 26, wherein the peracetic acid solution is prepared on a site having a point-of-use.

45. A non-equilibrium solution of peracetic acid made by the method of claim 7 for use as a disinfectant or sanitizer.

46. The solution of claim 45 for clean-in-place pipeline and equipment cleaning.

47. The solution of claim 45 for use in washing fruits and vegetables.

48. The solution of claim 45 for use in the treatment of meat, poultry, and seafood.

49. A method for sanitizing a surface, which comprises generating a non-equilibrium solution of peracetic acid comprising:

peracetic acid, hydrogen peroxide, triacetin, 1,2,3-propanetriol, a source of an alkali metal or earth alkali metal hydroxide, and water.

50. A non-equilibrium solution of peracetic acid, comprising:

a. peracetic acid;

b. hydrogen peroxide;

c. triacetin;

d. 1,2,3-propanetriol;

e. an aqueous source of an alkali metal or earth alkali metal hydroxide; and

f. water.

51. The solution of claim 50, wherein said solution has a pH of about 11.2 to about 13.37.

52. The solution of claim 50, wherein said peracetic acid is about 1% to about 7.1%.

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

a. providing water;

b. introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide and aqueous hydrogen peroxide to the water;

c. mixing the liquid acetyl precursor 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.

54. The method of claim 53, wherein the liquid acetyl precursor is triacetin defining a hydrogen peroxide-triacetin solution.

55. The method of claim 53, wherein the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced simultaneously.

56. The method of claim 53, wherein the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced sequentially with either one first.

57. The method of claim 53, wherein the provided water is an aqueous stream.

58. The method of claim 53, wherein the provided water is contained in a mixing tank or other vessel.

59. The method of claim 54, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

60. The method of claim 59, wherein the sodium hydroxide is about 1.82% to about 7.28%.

61. The method of claim 53, wherein step (d) is performed simultaneously with step (b).

62. The method of claim 53, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

63. The method of claim 62, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

64. The method of claim 63, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

65. The method of claim 60, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

66. The method of claim 53, wherein said steps (a) through (e) are performed on a continuous basis.

67. The method of claim 53, wherein said steps (a) through (e) are performed on an intermittent basis.

68. A method of generating a non-equilibrium solution of peracetic acid on a site having a point-of-use, comprising:

a. providing water on a site;

b. providing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide and aqueous hydrogen peroxide on the site having a point-of-use;

c. introducing the liquid acetyl precursor and the aqueous hydrogen peroxide to the water;

d. mixing the aqueous hydrogen peroxide and the liquid acetyl precursor with the water to form a mixture;

e. providing an aqueous source of an alkali metal or earth alkali metal hydroxide water on the site having the point-of-use;

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

g. forming a reaction medium comprising a non-equilibrium solution of peracetic acid for use at the point-of-use.

69. The method of claim 68, wherein the liquid acetyl precursor is triacetin.

70. The method of claim 68, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

71. The method of claim 70, wherein the sodium hydroxide is about 1.82% to about 7.28%.

72. The method of claim 68, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

73. The method of claim 72, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

74. The method of claim 68, further comprising, after step (g), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

75. The method of claim 72, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

76. The method of claim 71, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

77. An on site non-equilibrium peracetic acid generation system, comprising:

a first container comprising a first solution wherein said first solution comprises:

aqueous hydrogen peroxide;

a liquid acetyl precursor that is soluble in said aqueous hydrogen peroxide;

a trace amount of peracetic acid; and

water;

a second container comprising a second solution wherein said second solution comprises:

an aqueous source of an alkali metal or earth alkali metal hydroxide; and

means for mixing the first solution, water, and the second solution to generate a non-equilibrium peracetic acid solution.

78. A freely-flowable solid composition, comprising:

a. a liquid acetyl precursor;

b. a water-soluble solid source of hydrogen peroxide; and

c. a water-soluble solid source of alkalinity.

79. The composition of claim 78, wherein said liquid acetyl precursor is triacetin.

80. The composition of claim 79, wherein said triacetin is about 0.99% to about 8.45%.

81. The composition of claim 78, wherein said solid source of hydrogen peroxide is sodium percarbonate and is about 13% to about 54% of the total.

82. The composition of claim 78, wherein said solid source of alkalinity is about 24% to about 44% of the total.

83. A method of making a solid composition for bleaching and stain removal, comprising:

forming a homogenous freely-flowable solid by blending a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity.

84. The method of claim 83, wherein the liquid acetyl precursor is triacetin.

85. The method of claim 84, wherein the triacetin is about 0.99% to about 8.45%.

86. The method of claim 83, wherein the solid source of hydrogen peroxide is about 13% to about 54%.

87. The composition of claim 83, wherein the solid source of alkalinity is about 24% to about 44% of the total.

88. The method of claim 83, further comprising adding a metal chelating agent.

89. The method of claim 83, further comprising adding a surfactant.

90. The method of claim 83, further comprising adding a compound to sequester water hardness.

91. The method of claim 83, further comprising adding an inert solid filler.

## Abstract

Methods and compositions for the generation of a peroxyacetic acid sanitizer in proximity to the point-of-use are disclosed. These methods comprise introducing a hydrogen peroxide-acetyl 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 the 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 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.

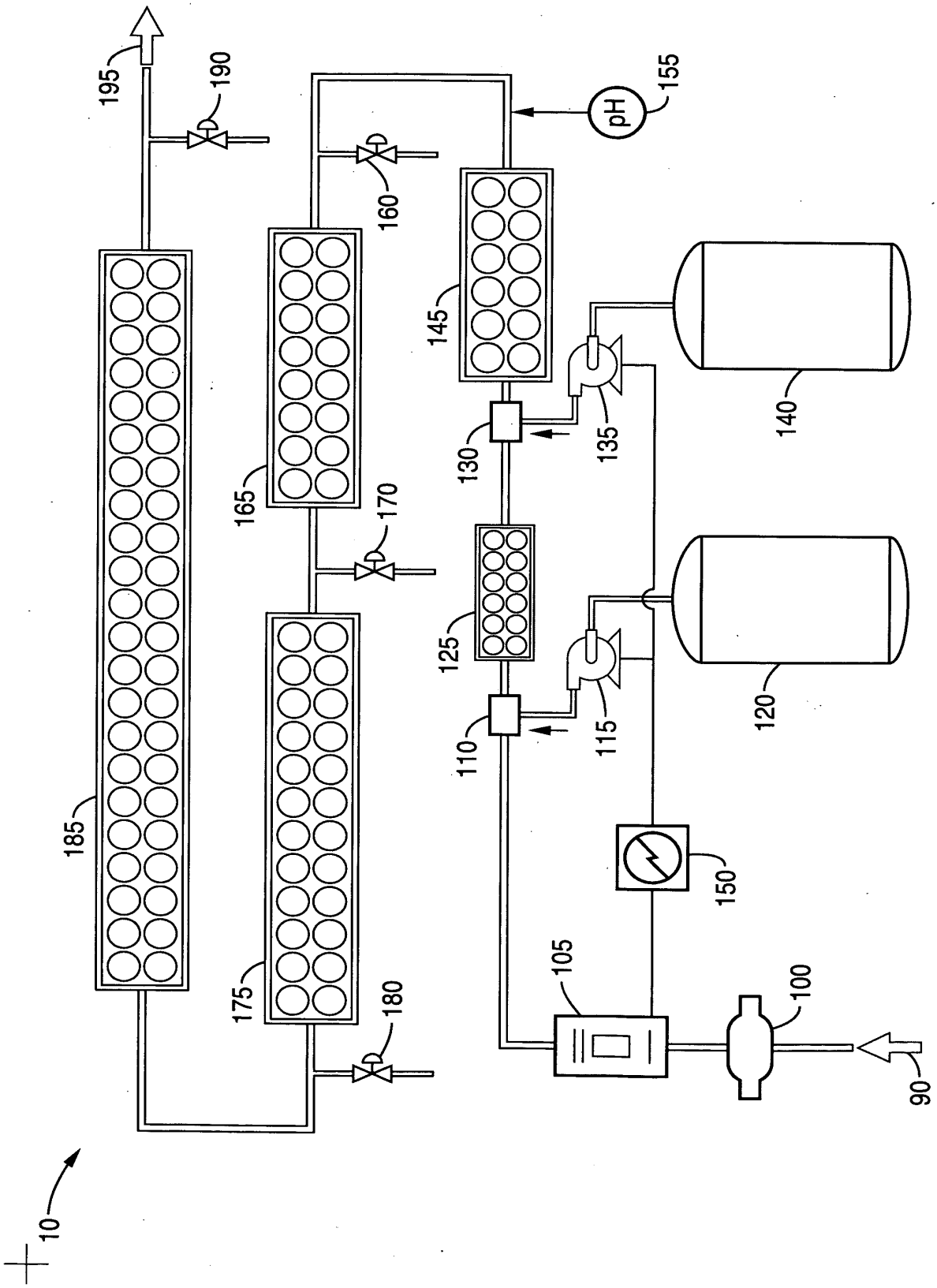

195
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FIG. 1

Exp. Mail EV 419585747 US

**Practitioner's Docket No.** 8568/17669 **PATENT**

# COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

## TYPE OF DECLARATION

This declaration is of the following type:

*(check one applicable item below)*

☒ original.

☐ design.

*NOTE: With the exception of a supplemental oath or declaration submitted in a reissue, a supplemental oath or declaration is not treated as an amendment under 37 CFR 1.312 (Amendments after allowance). M.P.E.P. § 714.16, 7th Edition.*

☐ supplemental.

*NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.*

☐ national stage of PCT.

*NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.*

*NOTE: See 37 C.F.R. § 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.*

☐ divisional.

☐ continuation.

*NOTE: Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. § 1.53(b) (application filing requirements — nonprovisional application).*

☐ continuation-in-part (C-I-P).

## INVENTORSHIP IDENTIFICATION

*WARNING: If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor *(if only one name is listed below)* or an original, first and joint inventor *(if plural names are listed below)* of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

## TITLE OF INVENTION

Methods and Compositions for the Generation of Peracetic Acid On Site at the Point-of-Use

## SPECIFICATION IDENTIFICATION

the specification of which:

*(complete (a), (b), or (c))*

(a) ☒ is attached hereto.

*NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:*

*"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;*

*"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or*

*"(3) name of inventor(s), and title which was on the specification as filed."*

*Notice of July 13, 1995 (1177 O.G. 60).*

(b) ☐ was filed on _____, as ☐ Serial No. 0 /_____

and was amended on _____ *(if applicable).*

*NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. § 1.67.*

*NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:*

*"(A) application number (consisting of the series code and the serial number, e.g., 08/123,456);*

*"(B) serial number and filing date;*

*"(C) attorney docket number which was on the specification as filed;*

*"(D) title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or*

*"(E) title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number, e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."*

*M.P.E.P. § 601.01(a), 7th Ed.*

(c) ☐ was described and claimed in PCT International Application No. _____, filed on _____ and as amended under PCT Article 19 on _____ *(if any).*



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## SUPPLEMENTAL DECLARATION (37 C.F.R. § 1.67(b))

*(complete the following where a supplemental declaration is being submitted)*

☐ I hereby declare that the subject matter of the

☐ attached amendment

☐ amendment filed on _____

was part of my/our invention and was invented before the filing date of the original application, above-identified, for such invention.

## ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

*(also check the following items, if desired)*

☒ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 C.F.R. § 1.98.

## PRIORITY CLAIM (35 U.S.C. §§ 119(a)-(d), (f) 172, and 365(a) and (b))

*NOTE: 37 C.F.R. § 1.55 Claim for foreign priority.*

*"(a) An applicant in a nonprovisional application may claim the benefit of the filing date of one or more prior foreign applications under the conditions specified in 35 U.S.C. 119(a) through (d) and (f), 172, and 365(a) and (b).*

*(1)(i) In an original application filed under 35 U.S.C. 111(a), the claim for priority must be presented during the pendency of the application, and within the later of four months from the actual filing date of the application or sixteen months from the filing date of the prior foreign application This time period is not extendable. The claim must identify the foreign application for which priority is claimed, as well as any foreign application for the same subject matter and having a filing date before that of the application for which priority is claimed, by specifying the application number, country (or intellectual property authority), day, month, and year of its filing. The time period in this paragraph does not apply to an application for a design patent.*

*(ii) In an application that entered the national stage from an international application after compliance with 35 U.S.C. 371, the claim for priority must be made during the pendency of the application and within the time limit set forth in the PCT and the Regulations under the PCT."*

*(2) The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. 119(b) or PCT Rule 17 must, in any event, be filed before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by the processing fee set forth in § 1.17(i), but the patent will not include the priority claim unless corrected by a certificate of correction under 35 U.S.C. 255 and § 1.323*

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

*(complete (d) or (e))*

(d) ☒ no such applications have been filed.

(e) ☐ such applications have been filed as follows.

*NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.*

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)**

| COUNTRY (OR INDICATE IF PCT) | APPLICATION NUMBER | DATE OF FILING (day, month, year) | PRIORITY CLAIMED UNDER 37 USC 119 |
|---|---|---|---|
| | | | ☐ YES NO ☐ |
| | | | ☐ YES NO ☐ |
| | | | ☐ YES NO ☐ |
| | | | ☐ YES NO ☐ |
| | | | ☐ YES NO ☐ |

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)**
(35 U.S.C. § 119(e))

*NOTE: 35 U.S.C. 119(e)(1) requires that a nonprovisional application be filed within twelve months of the filing date of the provisional application for the nonprovisional application to claim the benefit of the filing date of the provisional application. Under 35 U.S.C. 21(b) and 119(e)(3), if this twelve-month period expires on a non-business day, it is extended to expire on the next business day.*

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

| PROVISIONAL APPLICATION NUMBER | FILING DATE |
|---|---|
| _____ /_____ | _____ |
| _____ /_____ | _____ |
| _____ /_____ | _____ |

**CLAIM FOR BENEFIT OF EARLIER US/PCT APPLICATION(S) UNDER 35 U.S.C. § 120**

☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN PART (C-I-P) APPLICATION.

**ALL FOREIGN APPLICATION(S), *IF ANY*, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

_____

_____

_____

*NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.*

## POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

*(list name and registration number)*

Audrey A. Millemann (Reg. No. 44,942)

*(check the following item, if applicable)*

☐ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

*NOTE: "Special care should be taken in continuation or divisional applications to ensure that any change of correspondence address in a prior application is reflected in the continuation or divisional application. For example, where a copy of the oath or declaration from the prior application is submitted for a continuation or divisional application filed under 37 CFR 1.53(b) and the copy of the oath or declaration from the prior application designates an old correspondence address, the Office may not recognize, in the continuation or divisional application, the change of correspondence address made during the prosecution of the prior application. Applicant is required to identify the change of correspondence address in the continuation or divisional application to ensure that communications from the Office are mailed to the current correspondence address. 37 CFR 1.63(d)(4)." § 601.03, M.P.E.P., 7th Edition.*

| **SEND CORRESPONDENCE TO** | **DIRECT TELEPHONE CALLS TO:** *(Name and telephone number)* |
|---|---|
| ☒ Address<br>Audrey A. Millemann<br>Weintraub Genshlea Chediak<br>400 Capitol Mall, 11th Floor<br>Sacramento, CA 95814 | Audrey A. Millemann<br>(916) 558-6033 |
| ☐ Customer Number _____ | |

*(complete the following if applicable)*

Since this filing is a ☐ continuation ☐ divisional there is attached hereto a Change of Correspondence Address so that there will be no question as to where the PTO should direct all correspondence.

## DECLARATION

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

## SIGNATURE(S)

*NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other documents.*

*NOTE: Each inventor must be identified by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and by his/her residence, post office address and country of citizenship. 37 CFR § 1.63(a)(3).*

*NOTE: Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.63(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997.*

*WARNING: MPEP, § 409.03(b), 8th Edition: "Where an application is executed by one other than the inventor, the declaration required by 37 CFR 1.63 must state the full name, residence, post office address, and citizenship of the nonsigning inventor. Also, the title or position of the person signing must be stated if signing on behalf of a corporation under 37 CFR 1.47(b)."*

**Full name of sole or first inventor**

Michael (GIVEN NAME) S. (MIDDLE INITIAL OR NAME) Harvey (FAMILY (OR LAST NAME))

**Inventor's signature** Michael S Harvey

**Date** March 22 2011 **Country of Citizenship** U.S.

**Residence** Modesto, California

**Post Office Address** 712 Faust Road

Modesto, California 95358

**Full name of second joint inventor, if any**

Jonathan (GIVEN NAME) N. (MIDDLE INITIAL OR NAME) Howarth. (FAMILY (OR LAST NAME))

**Inventor's signature** Jonathan N. Howarth

**Date** March 22 2011 **Country of Citizenship** G.B.

**Residence** Modesto, California

**Post Office Address** 1848 Scenic Drive

Modesto, California 95355

**Full name of third joint inventor, if any**

(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST NAME))

**Inventor's signature**

**Date** **Country of Citizenship**

**Residence**

**Post Office Address**



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*(check proper box(es) for any of the following added page(s) that form a part of this declaration)*

☐ **Signature** for fourth and subsequent joint inventors. *Number of pages added* _____

• • •

☐ **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. ***Number of pages added*** _____.

• • •

☐ **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. ***Number of pages added*** _____.

• • •

☐ Added page for **signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

• • •

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

• • •

☐ Authorization of practitioner(s) to accept and follow instructions from representative.

• • •

*(if no further pages form a part of this Declaration, then end this Declaration with this page and check the following item)*

☒ **This declaration ends with this page.**

PATENT APPLICATION SERIAL NO._____

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE
FEE RECORD SHEET

03/25/2011 MBELETE1 00000056 501176 13065553

| | | |
|---|---|---|
| 01 FC:2011 | 165.00 | DA |
| 02 FC:2111 | 270.00 | DA |
| 03 FC:2311 | 110.00 | DA |
| 04 FC:2201 | 880.00 | DA |
| 05 FC:2202 | 1846.00 | DA |

PTO-1556
(5/87)

*U.S. Government Printing Office: 2002- 489-267/69033

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| APPLICATION NUMBER | FILING or 371(c) DATE | GRP ART UNIT | FIL FEE REC'D | ATTY.DOCKET.NO | TOT CLAIMS | IND CLAIMS |
|---|---|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | 1761 | 3271 | 8568/17669 | 91 | 11 |

**CONFIRMATION NO. 2262**

Audrey A. Millemann
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**FILING RECEIPT**

*OC000000047044286*

Date Mailed: 04/13/2011

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

**Applicant(s)**

Michael S. Harvey, Modesto, CA;
Jonathan N. Howarth, Modesto, CA;

**Power of Attorney:**
Audrey Millemann--44942

**Domestic Priority data as claimed by applicant**

**Foreign Applications** (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)

**If Required, Foreign Filing License Granted:** 04/08/2011

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 13/065,553**

**Projected Publication Date:** 09/27/2012

**Non-Publication Request:** No

**Early Publication Request:** No
** **SMALL ENTITY** **

**Title**

Methods and compositions for the generation of peracetic acid on site at the point-of-use

**Preliminary Class**

510

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## PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 13/065,553

### APPLICATION AS FILED - PART I

| FOR | (Column 1) NUMBER FILED | (Column 2) NUMBER EXTRA | SMALL ENTITY RATE($) | SMALL ENTITY FEE($) | OR | OTHER THAN SMALL ENTITY RATE($) | OTHER THAN SMALL ENTITY FEE($) |
|---|---|---|---|---|---|---|---|
| BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | 165 | | N/A | |
| SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | 270 | | N/A | |
| EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | 110 | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | 91 minus 20 = | * 71 | x 26 = | 1846 | OR | | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | 11 minus 3 = | * 8 | x 110 = | 880 | | | |
| APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $270 ($135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | 0.00 | | | |
| MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | | 0.00 | | | |
| * If the difference in column 1 is less than zero, enter "0" in column 2. | | | TOTAL | 3271 | | TOTAL | |

### APPLICATION AS AMENDED - PART II

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

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

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

05-14-12 IEJ

Doc Code: TRAN.LET

Document Description: Transmittal Letter

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PTO/SB/21 (07-09)
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# TRANSMITTAL FORM

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| | |
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| Total Number of Pages in This Submission | 239 |

| | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1761 |
| Examiner Name | |
| Attorney Docket Number | 8568/17669 |

## ENCLOSURES *(Check all that apply)*

- ☐ Fee Transmittal Form
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- ☐ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
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- ☑ Information Disclosure Statement
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- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
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- ☐ Status Letter
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  1. 4 Foreign Patent
  2. 5 Non Patent Literature Documents
  3. Return card

Remarks

## SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

| | | | |
|---|---|---|---|
| Firm Name | Weintraub Genshlea Chediak Tobin & Tobin | | |
| Signature | Audrey A. Millemann | | |
| Printed name | Audrey A. Millemann | | |
| Date | May 10, 2012 | Reg. No. | 44,942 |

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| Signature | Audrey A. Millemann | | |
| Typed or printed name | Audrey A. Millemann | Date | May 10, 2012 |

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

| | | |
|---|---|---|
| Applicants: | Michael S. Harvey, et al. | |
| Serial No.: | 13/065,553 | Art Unit: 1761 |
| Filing Date: | March 24, 2011 | |
| For: | Methods and Compositions for the Generation of Peracetic Acid on Site at the Point-of-Use | |

May 10, 2012
Sacramento, California 95814

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Commissioner for Patents
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Alexandria, VA 22313-1450

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Pursuant to Rules 1.97 and 1.98, Applicants submit herewith copies of patents, publications, or other information of which Applicants are aware, as listed on the accompanying Form 1449, which Applicants believe may be material to the examination of this application and with respect to which there may be a duty to disclose.

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The filing of this information disclosure statement and accompanying Form 1449 shall not be construed as an admission against interest in any manner. (Notice of January 9, 1992, 1135 O.G. 13-25, at 25.)

Respectfully submitted,

Michael S. Harvey, et al.

By: Audrey A. Millemann

Audrey A. Millemann (Reg. No. 44,942)
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*(Use as many sheets as necessary)*

Sheet 1 of 2

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1761 |
| Examiner Name | |
| Attorney Docket Number | 8568/17769 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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| | | US- 3,956,159 | 05-11-1976 | Jones | |
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| | | US- | | | |

**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3]-Number[4]-Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
|---|---|---|---|---|---|---|
| | 1 | EP 0 563 460 B1 | 07-01-1998 | The Procter & Gamble Co. | | |
| | 2 | WO 01/46519 A1 | 06-28-2001 | Warwick International | | |
| | 3 | WO 2008/140988 A1 | 11-20-2008 | Danisco US Inc. | | |
| | 4 | WO 2010/005607 A2 | 01-14-2010 | Electron Research & Dev. | | |
| | | | | | | |
| | | | | | | |

| Examiner Signature | | Date Considered | |
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Sheet 2 of 2

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1761 |
| Examiner Name | |
| Attorney Docket Number | 8568/17669 |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | T[2] |
|---|---|---|---|
| | 1 | LEVENEUR, et al., "Interaction of Instrinsic Kinetics and Internal Mass...Acids," Chemical Engineering Science 64 (2009) pp.4101-4114 | |
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| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

| Examiner Signature | | Date Considered | |
|---|---|---|---|

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(71) Applicant *(for all designated States except US)*: WARWICK INTERNATIONAL GROUP LIMITED [GB/GB]; Mostyn, Holywell, Flintshire CH8 9HE (GB).

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(74) Agents: GODDARD, David, John; Harrison Goddard Foote, Orlando House, 11c Compstall Road, Marple Bridge, Stockport SK6 5HH___ et al. (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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**Published:**
— *With international search report.*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/46519 A1

(54) Title: PEROXYACID DELIVERY PROCESS

(57) Abstract: In a peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution (5) and bleach activator (10) mixed together in a tank (1), the pH of the mixture is adjusted by the addition or injection of an alkaline material (16) selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions such as are provided by an in-line mixer (14) within which the Froude number is at least 1. Preferably the output of mixer (14) is fed though a pipe (18), which may be coiled through a cooling tank (19) for heat dissipation, to provide a residence time of 4 to 25 minutes for completion of the reaction without degradation of the product, which may be used for pulp bleaching. Preferably an excess of hydrogen peroxide is present, and sequestrant (3) is incorporated in the peroxide-activator mixture.

# Peroxyacid Delivery Process

This invention relates to peroxyacid delivery processes, in particular to processes in which a peroxyacid is formed by the reaction of hydrogen peroxide solution with a bleach activator. Herein the term "peroxyacid" is intended to include the anion, the relative amounts of the two species being depending on the pH. The peroxyacid is useful for the bleaching of wood or non-wood pulp under alkaline conditions.

The invention also encompasses the formation and delivery of a bleaching solution that contains a mixture of peroxyacid and hydrogen peroxide by the reacting under alkaline conditions an agglomerate or crystalline tetraacetylethylenediamine, commonly known as as TAED, with excess hydrogen peroxide. The bleaching solution is useful for the bleaching of wood or non-wood pulp under alkaline conditions.

Oxygen based bleaching is used because of its environmental benefits and oxidising power. Hydrogen peroxide is increasingly being used in oxygen based pulp bleaching. It has been proposed to use peroxyacid, especially peracetic acid, as a bleach or disinfectant. Both the on site generation of peracetic acid from carboxylic acid and hydrogen peroxide and the distribution of distilled or equilibrium peracetic acid presents risks which many potential users find unacceptable.

It has been proposed to solve this problem by reacting hydrogen peroxide with a bleach activator to generate a peroxyacid based oxygen bleaching species *in situ* to facilitate pulp bleaching and delignification.

Peroxyacid delivery processes using bleach activators have generally formed the peroaxyacid in the presence of the substrate to be bleached or disinfected.

The "pre-reaction" of a bleach activator with hydrogen peroxide for the formation of peroxyacid is claimed in copending application PCT/GB/9903178. The TAED bleach activator is pre-reacted batchwise with hydrogen peroxide, adjusted to a suitable alkaline pH and then pumped to the point of use. Batch reactions require bulky equipment, especially for larger duty operations. Furthermore the creation of a



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large batch of peroxyacid may result in wastage if a problem prevents it being used for bleaching within a few hours.

TAED is a fine white crystalline powder. Use of TAED powder in a pre-reaction with hydrogen peroxide to form a bleaching solution for use in a bleaching process is undesirable for a number of reasons. Firstly it would not have the required free flow properties to be dosed effectively from a hopper. Secondly it would require special equipment to control dust levels. Thirdly it would not mix well with hydrogen peroxide solution and would have poor dispersing dissolution characteristics. These problems can be overcome by use of an agglomerated product.

TAED powder may be agglomerated using one or more binders provided specifically for this purpose, a commonly used binder being sodium carboxymethylcellulose (CMC). Alternatively a binding function in a TAED bleaching composition may be provided by an additional component incorporated for other purposes, or by an appropriate treatment such as extrusion where no specific binder is present. For use in the present invention, a preferred agglomerated product contains at least 50% TAED, and typically it contains from about 80 to about 90% TAED with the remainder being made up of any binder or binder system and optional disintegration and dispersion aids, together with other minor components, such as pigments, colorants and sequestrants. Where no binder is specifically added for the purpose, more than 90% TAED may be present in the agglomerate.

Use of bleach activator agglomerates containing a sodium carboxymethylcellulose or other conventional binder for large-scale reactions leads to problems. Firstly, as is the case with sodium carboxymethylcellulose, the binder may be insoluble under the pH and temperature conditions under which agglomerates may need to be pre-reacted with the hydrogen peroxide solution. Secondly the binder may react with the caustic soda added to adjust the alkalinity of the pre-reaction mixture and/or the pulp. Additionally, suspension of agglomerates in peroxide can form scum, which is unacceptable for processes, such as pulp bleaching, where residual solid matter must be avoided. Conventional binders may give rise to poor bleaching and may even form coloured species under the extremes of one or more of temperature, pressure



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and residence time encountered in some processes. It has also been found that agglomerates with conventional binder systems do not disperse fast enough or wet fast enough in the low ionic medium of a pre-reaction process.

It would be desirable to have a safe, continuous process for on site generation of peroxyacid with low capital cost and short residence time.

The present invention provides a peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution and bleach activator characterised in that the pH of a mixture of hydrogen peroxide solution and bleach activator is adjusted by the addition or injection of an alkaline material selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions provided by an in-line mixer within which the Froude number is at least 1, or by another mixer or combination of mixers providing an equivalent speed and intimacy of mixing. Where magnesium oxide is mentioned, this encompasses the hydrated product, irrespective of whether this is defined as magnesium oxide or magnesium hydroxide.

A definition of the dimensionless densiometric Froude number is given by:

$$\text{Froude Number} = \frac{v^2}{g.L}$$

where:

| | | |
|---|---|---|
| $v$ | = | Flow velocity (m/s) |
| $g$ | = | gravitational acceleration (m/s2) |
| $L$ | = | characteristic dimension of the system (m) |
| | = | $(\Delta\rho/\underline{\rho}).d_h.\varepsilon^2)$ |
| $\Delta\rho$ | = | difference in density between components being mixed |
| $\underline{\rho}$ | = | mean density of the components being mixed |
| $d_h$ | = | hydraulic diameter of the mixing unit (m) |
| $\varepsilon$ | = | void fraction of mixing unit. |

In-line mixers can enable the injection of the alkaline material in an essentially enclosed part of the system under continuous flow conditions between the supply of



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mixed hydrogen peroxide and activator and a continuous supply outlet for the peroxyacid containing product. Of particular and preferred use are static in-line mixers containing elements to result in turbulent mixing of the alkaline material and the mixed hydrogen peroxide and activator to give a Froude number of more than 4, preferably more than 10 and most preferably more than 20.

However, the invention encompasses the use of other types of in-line mixer, and of other mixers capable of being inserted between the supply of mixed hydrogen peroxide and activator and a continuous supply outlet for the peroxyacid containing product, including tank type mixers. If necessary, a single mixer giving a lower Froude number or equivalent effect may be used in association with one or more further mixers, e.g. supplementary kinetic or dynamic mixers or agitators to provide the requisite speed and intimacy of mixing. However, a single mixer is at present preferred.

In a preferred embodiment the alkaline material is sodium hydroxide. Addition of sodium hydroxide solution without sufficiently vigorous mixing causes gassing off of hydrogen peroxide and loss of yield of the peroxyacid. Adjustment of the pH to about 8 to about 9.5, e.g. by use of sufficient sodium hydroxide, is recommended for greater than 90% yield based on TAED.

Advantageously an excess of sodium hydroxide. which equates to at least to 1 part by weight sodium hydroxide to 4 parts by weight TAED is used. This gives a pH of greater than 8 and gives better peracetate anion yield, based on TAED, than in the case if less sodium hydroxide is used. Greater sodium hydroxide excesses up to and greater than 1 part by weight sodium hydroxide to 3 parts TAED or even 1 part sodium hydroxide to 2 parts TAED can also be used. The ideal yield for the peracetate anion production is preferably >85% TAED conversion and most preferably >90% TAED conversion (based on two acetyl groups released per TAED).

The reaction mixture is preferably pumped along a reaction pipe downstream of the vigorous mixer(s) with a residence time of between 4 and 25 min.



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The premixing of the bleach activator and the hydrogen peroxide solution can be done in any suitable continuous or semi-batch operation. Agglomeration of the activator facilitates accurate dosing and also allows for easy recovery from accidental spillage. The bleach activator may be any one or mixtures of more than one acetyl donor. The process is particularly suitable for use with agglomerated TAED.

Activators generating peracids other than peracetic acid may be used but are not preferred. Specific activators, which are available for use in the invention, are tetraacetylethylenediamine (TAED), pentaacetyl glucose (PAG), tetraacetylglycolouril (TAGU), N-acetyl caprolactam, N-benzoyl caprolactam and triacetylethanolamine. Of these TAED is preferred because it gives the most cost-effective release of acetyl groups: it releases two such groups per molecule.

Binders and dispersing systems for the TAED agglomerate may be selected to suit the process. Preferred agglomerates comprise: TAED; a water soluble binder or binder system, preferably polyvinyl alcohol (PVOH); a dispersing system comprising a wetting agent which is a low foaming and does not discolour on exposure to temperatures of up to 120°C and optionally a salt, preferably sodium acetate, which is highly soluble in hydrogen peroxide. The binder or binder system preferably comprises less than 1.2%, preferably less than 0.5% CMC, and most preferably none at all.

The agglomerate preferably comprises: a TAED agglomerate with average particle size in the range of 5 to 2000 micron having a binder or binder system comprising less than 1.2% preferably less than 0.5% CMC, most preferably none at all; and 2-8% of anionic surfactant which can be dried to a solid and other ingredients which are non precipitating over the pH range of 5-10, the binder or binder system further being completely compatible with the pulp bleaching process and preferably readily biodegradable. For processing reasons the agglomerate may comprise up to 1.2%, preferably 0.1 to 0.5% by weight based on the dry agglomerate of a co-binder, such as sodium carboxymethylcellulose (CMC). However, agglomerates without any CMC are preferred.



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Preferably the anionic surfactant is incorporated at a level of 1 to 6% by weight based on the dry agglomerate, most preferably about 2.5%.

Other additives such as flow aids, sequestrants, pH adjusting components, diluents and the like may also be included in the agglomerate if required. The inclusion of one or more sequestrants is particularly advantageous, as these enable any transition metals in the water and alkali used to adjust the pH to be rendered non-catalytic for the decomposition of the hydrogen peroxide. If they are not added as part of the agglomerate they may be added separately, or to the hydrogen peroxide.

The agglomerates may be manufactured using any process known to those skilled in the art e.g. mixing TAED powder and a solution of surfactant to form agglomerates and drying the agglomerates so formed.

The concentration of hydrogen peroxide in the pre-reaction mixture (prior to pH adjustment) is normally in the range of 0.1 to 60% preferably 0.2 to 30% w/v. A typical level will be 3%. The amount of bleach activator used in the pre-reaction mixture should be in the range 0.001 to 20 g/l based on the theoretical dose to dry pulp. When TAED is used as the bleach activator we have found that use of large concentrations of TAED leads to an undesirable exothermic reaction and the maximum concentration that should be used is 10%, preferably 5% and most preferably less than 2%.

An excess of hydrogen peroxide, over the acetyl groups that are released from the bleach activator, is used. The mole ratio of peroxide to releasable acetyl groups is preferably more than 2:1, more preferably at least 3:1, and most preferably at least 3.35:1. It may be 10:1 or more, but it is preferably no greater than 5:1, more preferably no greater than 4:1.

As the per-acetic anion release between TAED and hydrogen peroxide solution takes at least 4 minutes to release >90% per-acetic anion after addition of the sodium hydroxide (alkaline material) the bleaching solution is provided with a residence time of at least 4 minutes, preferably by being passed through a reaction pipe or other vessel. In the latter case, the residence time is conveniently adjusted to suit the flow



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rate by adding or subtracting lengths of pipe. The residence time for the reaction pipe is preferably no more than about 25 minutes.

The process is adaptable to any location and the reaction pipe length can be adapted according to the distance from the dosing point, with bore and length of the reaction pipe and flow rate being conjointly selected to give the correct retention time.

The activator input feed rate may be controlled via a flow meter feedback loop to the feed system, e.g. a volumetric feeder. The control point or measurement point may be located near the outlet of the reaction pipe. A pH probe near the outlet of the reaction pipe may be used to control the input rate of the alkaline material, e.g. a concentrated sodium hydroxide solution, such as one with a weight concentration of more than 3, preferably more than 5, more preferably more than 10, still more preferably more than 20 and most preferably more than 40 weight percent (but preferably no more than 50 weight percent), or a magnesium oxide slurry.

Although a tank may be used to provide at least part of the reaction capacity downstream of the vigorous or in-line mixer if desired, the use of a reaction pipe may have advantages over a tank. As with the use of an in-line mixer, because the system is then enclosed, exposure of an operator to peracetic anion solution is reduced. Furthermore, making the reaction pipe into a coil and applying cooling to it can dissipate heat. In addition the use of a reaction pipe gives more control over residence time than would be obtained from a tank, thus enabling greater control over the bleach solution concentration at the exit from the reaction pipe and therefore the point of delivery to the bleaching process.

The addition of untreated water to the bleaching solution will introduce transition metal ions. These are able to catalyse the decomposition of hydrogen peroxide. Treating the water to remove the ions or to render them inactive is necessary. A preferred treatment is to use a sequestrant. Any sequestrant may be used, including EDTA, DTPA (diethylenetriamine penta-acetic acid) and other sequestrants that do not contain phosphorous, but a phosphonate stabiliser is preferred. Preferred sequestrants are selected from the group comprising pentamethylene phosphonic acid and diethylenetriamine penta-(methylene phosphonic acid). The ratio of sequestrant to water is in the range 1:100 to 1:10000 parts by weight.



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An advantage of a continuous peroxyacid generating system is that it eliminates the need for a specific acid addition step that previous batch systems have required to lower the pH of the solution in the batch tank. Nevertheless, if the necessity should ever arise, it is possible to add acid to the pulp bleaching tank.

A further advantage of generating the peroxyacid continuously is that it may easily be controlled because it is operating as a steady state reaction.

Another advantage of the continuous process is that it can easily be scaled up without using correspondingly larger mixing tanks, that may take up too much space to enable the equipment to be added into an existing manufacturing facility.

Further features and advantages of the invention will become clear upon a reading of the appended claims, to which the reader is referred, and to the following description made with reference to the accompanying drawing and examples in which:

Figure 1 is a schematic of a continuous peroxyacid generating system.

Figure 1 shows a batch make-up tank 1. The tank is fed with water along delivery pipe 2. Sequestrant is dosed from tank 3 along sequestrant supply pipe 4. Hydrogen peroxide is dosed from tank 5 along peroxide supply pipe 6. Valves 7, 8 and 9 control the water, sequestrant and peroxide supplies respectively. Agglomerated TAED is held in a hopper 10 and fed to the tank 1 via a screw feeder 11. The contents of tank 1 are kept in suspension and mixed using an agitator 12. The outlet from tank 1 is fed by pump 13 to in-line mixer 14. The in-line mixer is also fed through pump 15 with caustic soda solution from tank 16. A control unit 17 controls valves 7, 8 and 9, screw feeder 11, and pumps 13 and 15. The output from the in-line mixer 14 enters a reaction pipe 18 which may be made up of a series of pipes, some of which may be coiled to allow for them to be put into a secondary container 19 which may have a cooling system 20. The reaction pipe 18 is connected into the bleaching process at its end 21.

The continuous process operates as follows: the control unit 17 opens valve 7 to allow approximately 100 kg of water to enter the batch make-up tank 1 along supply pipe 2. At the same time 0.2kg of sequestrant is dosed along pipe 4 by opening valve



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8 and agglomerated TAED also enters tank 1 from hopper 10 by operation of the screw feeder 11. This takes about 1 minute. Throughout the fill cycle the agitator 12 is in continuous operation. Towards the end of the cycle the hydrogen peroxide is dosed along line 6 when the controller 17 opens valve 9. At the end of this fill cycle the level in tank 1 is at its maximum. Pump 13 empties tank 1 continuously and at a defined lower level of liquid in tank 1, or a defined period of time, the fill cycle starts again. Alternatively in a modification continuous metering pumps deliver all the components on a continuous basis. In a more automated process for variable flow rates, the flow rate is sensed, for example near the output 21, and is used to control the continuous metering pumps.

The homogeneous mixture or suspension of TAED, hydrogen peroxide, water and sequestrant is continuously dosed by pump 13 through the in-line mixer 14 where sodium hydroxide is also dosed continuously via pump 15 in sufficient quantity to give the required pH at the end of the reaction, e.g. at or near the end 21 of pipe 18. Once an empirical relationship has been determined the controller 17 controls the sodium hydroxide delivery by controlling pump 15 according to the setting of pump 13 which in turn is set by the overall flow requirement. In an alternative process, pH is determined, for example at or near an end 21 of pipe 18, and is used to control pump 15.

The reaction requires at least 4 minutes after the in-line mixer to achieve greater than 85% TAED to peracetate anion conversion. This reaction time is achieved by pumping the mixture through reaction pipe 18. The length of the reaction pipe 18 is dependent on flow rate and pipe volume (pipe bore) and the required retention time.

The in-line mixer 14 creates turbulent flow, causing intimate mixing of the sodium hydroxide and the TAED/peroxide mixture which leads to the reaction progressing rapidly, no solids being visible immediately down stream of the in-line mixer. This contrasts sharply with the build up of solids that occurs in that area if the mixing element of the in-line mixer 14 is removed.



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**Examples 1 to 11** In these Examples sodium hydroxide addition was controlled according to the amount of TAED being used. Examples 1 to 6 were to assess the optimum ratio of sodium hydroxide to TAED. These examples used a 200m long reaction pipe of suitable diameter to give the required retention time. Comparative Example 7 was carried out to test the effectiveness of the in-line mixer in the system and was a repeat of Example 6 with the mixing element removed from the in-line mixer so that the sodium hydroxide was added directly to the slurry with no mixing at all. Throughout, it could be seen that the system was not effective because rapid de-gassing was occurring during the reaction and TAED crystals could be seen in the samples. Comparative example 7 gave a low peracetate anion release. To investigate this further the dimensionless densiometric Froude number was calculated for Example 6 to be 6.6 which contrasted with the much lower Froude number of 0.64 Comparative calculated for Comparative Example 7.

Comparative Examples 10 and 11 were a repeat of Example 1 except that Comparative Example 10 used powdered uncoated TAED and Comparative Example 11 used a CMC bound TAED agglomerate traditionally used in detergent formulations. Comparative Example 10 was a very poor producer of peracetate anion because the TAED could not be entrained without high shear agitation. When this agitation was applied, severe foaming occurred in the make-up tank. Comparative Example 11 did not produce any peracetate anion because the agglomerate foamed during mixing and did not become entrained in the batch tank.

The results of Examples 1 to 11 are given in Table 1. PAR is peracetic anion release, measures against the theoretical release based on the amount of TAED used. The results show that a TAED to sodium hydroxide ratio of less than or equal to about 4 to 1 is required to achieve greater than 85% Peracetate anion generation.

**Examples 12-15** To ensure that the Froude number had a significant effect on peracetic anion release more Examples with and without the in-line mixer (ILM) at different flow rates were carried out. The results are shown in Table 2. All these examples were carried out using a 200m reaction pipe.



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The peracid release at lower Froude numbers is less good than at higher Froude numbers. Using the in-line static mixer with an element designed to provide radial mixing increases the Froude number for a given flow rate (retention time).

**Table 1**

| Example | NaOH Parts | TAED Parts | Retention Mins. | ILM | Temp °C | PH Ave. | PAR% Ave. |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 4 | 10 | ✓ | 17 | 8.69 | 90 |
| 2 | 1 | 5 | 10 | ✓ | 17 | 8.39 | 81 |
| 3 | 1 | 3 | 10 | ✓ | 17 | 9.06 | 92 |
| 4 | 1 | 4 | 12 | ✓ | 17 | 8.61 | 92 |
| 5 | 1 | 4 | 8 | ✓ | 17 | 8.46 | 91 |
| 6 | 1 | 4 | 8 | ✓ | 22 | 8.43 | 90 |
| C7 | 1 | 4 | 10 | X | 17 | 8.82 | 77 |
| 8 | 1 | 24 | 6 | ✓ | 22 | 8.87 | 91 |
| 9 | 1 | 24 | 4 | ✓ | 17 | 8.93 | 87 |
| C10 | 1 | 24 | 10 | ✓ | 17 | 9.58 | 69 |
| C11 | 1 | 24 | 10 | ✓ | 17 | - | 0 |

**Table 2**

| Example | Retention Mins | ILM | Froude Number | PAR% Ave |
|---|---|---|---|---|
| 12 | 19 | ✓ | 1 | 66.1 |
| 13 | 19 | X | 0.18 | 51.9 |
| 14 | 6 | ✓ | 10.2 | 91.1 |
| 15 | 6 | X | 1.8 | 76.8 |



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CLAIMS

1. A peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution and bleach activator characterised in that the pH of a mixture of hydrogen peroxide solution and bleach activator is adjusted by the addition or injection of an alkaline material selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions provided by an in-line mixer within which the Froude number is at least 1, or by another mixer or combination of mixers providing an equivalent speed and intimacy of mixing.

2. A peroxyacid delivery process according to claim 1 in which said Froude number is greater than 4, preferably greater than 10 and most preferably greater than 20.

3. A peroxyacid delivery process according to claim 1 or claim 2 in which the reaction of the bleach activator and the hydrogen peroxide takes place in the presence of a sequestrant, preferably a phosphonate (phosphonic acid) stabiliser.

4. A peroxyacid delivery process according to any preceding claim in which after said addition or injection of alkaline material the reaction mixture is pumped along a pipe with a residence time of between 4 and 25 min.

5. A peroxyacid delivery process according any preceding claim in which the bleach activator is TAED.

6. A peroxyacid delivery process according to claim 5 in which the TAED is added as an agglomerate which contains at least 50 % by weight TAED.

7. A peroxyacid delivery process according to any preceding claim wherein the alkaline material is sodium hydroxide.

8. A peroxyacid delivery process according to claim 5 and claim 7, or claim 6 and claim 7, in which the weight ratio of sodium hydroxide to TAED is at least 1 to 4.



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# INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 00/04876

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C9/16 C07C407/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21C C07C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
CHEM ABS Data, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | C. LEDUC ET AL: APPITA J., vol. 51, no. 4, 1998, pages 306-310, XP000926194 whole document, in particular page 308, column 3 - page 309, column 1 | 1,5,7 |
| A | EP 0 456 032 A (HOECHST JAPAN LTD) 13 November 1991 (1991-11-13) whole document | 1,5,7 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 20 February 2001 | 07/03/2001 |

| Name and mailing address of the ISA | Authorized officer |
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Van Amsterdam, L |

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int .onal Application No
PCT/GB 00/04876

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | CA 2041468 A | 26-10-1991 |
| | | FI 911963 A | 26-10-1991 |
| | | NO 911626 A | 28-10-1991 |

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(54) **Acidic activated bleaching composition**

Durch Säure aktivierte Bleichzusammensetzung

Composition de blanchiment activée par un acide

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**EP-A- 0 125 781**

- **DATABASE WPIL Section Ch, Derwent Publications Ltd., London, GB; Class D25, AN 87-045571 [07] & JP-A-62 001 794 (KAO CORP.)**
- **DATABASE WPIL Section Ch, Derwent Publications Ltd, London, GB; Class D25, AN 87-046869 [07] & JP-A-62 004 794 (KAO CORP.)**

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EP 0 563 460 B1

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## Description

### Technical field

The present invention relates to bleaching compositions, mainly for use in laundry applications. The compositions according to the present invention, which comprise hydrogen peroxide as well as peracid precursors, are stable upon storage.

### Background

Bleaching compositions using hydrogen peroxide have been extensively described in the art. Such hydrogen peroxide bleaches have an advantage over chlorine bleaches in that they are environmentally more compatible. Another advantage is that they are "milder" bleaches. This latter advantage is especially significant in laundry applications as hydrogen peroxide bleaches are safer to fabrics.

A major drawback of hydrogen peroxide bleaches is that they are less active than chlorine bleaches at low temperatures which are often encountered in modern laundering applications. Thus, hydrogen peroxide bleach activators have been developed and have been extensively described in the art. These activators are mainly transition metals or peracid precursors. Peracid precursors react with hydrogen peroxide to yield peracids. Peracids are the "activated" bleaching compounds which are efficient at low temperatures.

A problem which occurs in the formulation of such "activated" hydrogen peroxide bleaching compositions is the difficulty to obtain a composition which is both chemically and physically stable. Indeed, such compositions of the prior art are either turbid suspensions of insoluble activators with good chemical stability, or clear compositions with poor chemical stability which causes significant and undesired oxygen release.

It has now been found that this problem could be addressed by formulating a bleaching composition comprising hydrogen peroxide, an organic peracid precursor selected from a specific class, e.g. glycol and glycerin esters, and by formulating said composition in a narrow, acidic pH range. The mildly acidic pH range allows for adequate chemical stability of both the hydrogen peroxide and the organic peracid precursor. The activation of hydrogen peroxide trough the formation of a peracid is enhanced by the pH raise which occurs upon dilution in the wash water, especially when a detergent composition bringing further alkalinity is also present in the wash water.

Glycol esters have been often described as solvents in detergent and bleaching compositions. Such compositions are described for instance in US-A-3 956 159. These compositions have a pH of 6.5 and above.

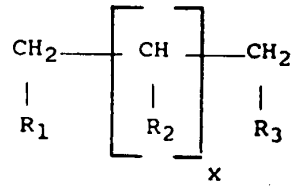
JP-A-62252500 (abstract) discloses bleaching compositions which comprise a bleach activator, including triacetin. These compositions are formulated at neutral or weakly basic pH.

Bleaching compositions for various applications, comprising triacetin are also disclosed in JP-A-62001792, JP-A-62001794 JP-A-62001796, and JP-A-61042600 (abstracts).

EP-A-125 781 discloses bleaching compositions comprising hydrogen peroxide and a particular peroxyacid generator like for example 1,1,5-triacetoxypent-4-ene, 1,1,5,5-tetraacetoxy pentane, the corresponding butene and butane compounds, ethylidene benzoate acetate and bis (ethylidene acetate) adipate.

### Summary of the invention

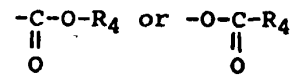
The compositions according to the present invention are clear aqueous bleaching compositions comprising hydrogen peroxide as well as an organic peracid precursor, characterized in that the compositions have a pH in the range of from 3.5 to 6, and that the organic peracid precursor is a compound according to the formula:



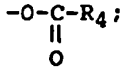
wherein x is 0 or 1, $R_1$, $R_2$, $R_3$ are independently selected from -H, -OH,



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where $R_4$ is $C_1$-$C_4$ alkyl, with the proviso that at least two of $R_1$, $R_2$ or $R_3$ are

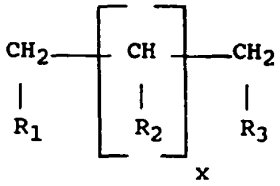


or mixtures thereof.

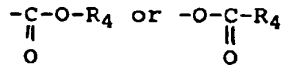
Detailed description of the invention

The compositions according to the present invention are clear aqueous liquid compositions which comprise hydrogen peroxide. Preferably, the compositions according to the present invention comprise from 0.5 % to 20 % by weight of the total composition of hydrogen peroxide, more preferably from 2 % to 15 %, most preferably from 4 % to 9%.

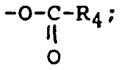
The compositions according to the present invention further comprise a specific organic peracid precursor according to the formula:



wherein x is 0 or 1, $R_1$, $R_2$, $R_3$ are independently selected from -H, -OH,



where $R_4$ is $C_1$-$C_4$ alkyl, with the proviso that at least two of $R_1$ $R_2$ or $R_3$ are



or mixtures thereof. All these compounds are well known chemicals which are commercially available or can be synthesized according to the chemical literature.

Preferred such peracid precursors for use in the compositions according to the present invention are selected from ethylene glycol diesters, triacetin and diacetin, or mixtures thereof. Particularly preferred compounds are triacetin and ethylene glycol diacetate. Tributyrin also displays excellent stability in the compositions according to the present invention but is less preferred because it is less soluble in the compositions according to the present invention.

The compositions according to the present invention typically comprise from 1 % to 15 % by weight of the total composition of such an organic peracid precursor, or mixtures thereof. The desired amount of organic peracid precursor can also be defined in relation to the amount of hydrogen peroxide in the composition. Accordingly, the compositions according to the present invention preferably comprise from 0.1 to 2 moles of organic peracid precursor per mole of hydrogen peroxide.

The compositions according to the present invention have a pH in the range of from 3.5 to 6, most preferably from 3.5 to 5, most preferably about 4. The pH of the composition can be adjusted and buffered with such chemicals as



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organic and inorganic acids which are stable to oxidation, citric acid, sulphuric acid, sodium hydroxide, ammonia and amines. Preferred buffer for use in the compositions according to the present invention is citric acid. It is essential that the pH of the composition remains within the above range as said range is critical to ensure adequate chemical stability of the hydrogen peroxide and of the specific organic peracid precursors used in the compositions according to the present invention.

The compositions according to the present invention may comprise surfactants. Preferred surfactants for use herein are well known anionic surfactants such as alkyl benzene sulphonates and alkyl sulfates, and/or nonionic surfactants such as ethoxylated and/or propoxylated alcohols. All surfactants for use herein must be resistant to oxidation by peracids and hydrogen peroxide, and are preferably water-soluble. The compositions according to the present invention can comprise from 0% to 30% by weight of the total composition of surfactants, preferably from 0.5 % to 15 %, most preferably from 2 % to 8 %.

The compositions according to the present invention may further comprise peroxide stabilizers such as stannates, 8-hydroxyquinoline, pyrophosphates and phosphonates. Chelating agents may also be useful in the context of the present invention; suitable chelants include EDTA, NTA and DETPA, picolinic and dipicolinic acids and amino polyphosphonates, although some of these are poorly environmentally compatible. Radical scavengers can also be used herein, such as butylated hydroxy toluene and other hindered hydroxy benzenes, or sodium benzoate. Butylated hydroxy toluene is a highly preferred ingredient as it has been observed that it stabilizes the peracid precursors according to the present invention, as well as hydrogen peroxide.

The compositions according to the present invention can also comprise such optional ingredients as whitening agents, dyes, builders, thickeners, hydrotropes, perfumes, all of which need to be compatible with the mildly acidic pH and the oxidizing environment of the compositions according to the present invention.

The compositions according to the present invention are further illustrated in the following examples.

Examples

The following compositions are made by mixing together the listed ingredients in the listed proportions.

| Ingredients: | % by weight: | | | | |
|---|---|---|---|---|---|
| | I | II | III | IV | |
| Hydrogen peroxide | 6.0 | 6.0 | 6.0 | 6.0 | |
| Na alkyl sulphate | 2.8 | 2.8 | 2.8 | 2.8 | |
| Triacetin | 4.0 | 5.0 | 4.0 | 4.0 | |
| Citric acid | 1.0 | 1.0 | 1.0 | 1.0 | |
| Na Stannate | 0.0015 | 0.0010 | 0.0015 | 0.0015 | |
| Na hydroxide | pH 4 | pH 4 | pH 3.5 | pH 5 | pH 4 |
| Water & minors | | | up to 100 % | | |

| Ingredients: | % by weight: | | | |
|---|---|---|---|---|
| | V | VI | VII | VIII |
| Hydrogen peroxide | 6.0 | 8.0 | 3.5 | 5.0 |
| Na alkyl sulphate | 2.8 | 2.0 | 4.0 | 3.5 |
| Triacetin | - | 3.0 | 5.0 | - |
| Ethylene glycol diacetate | 4.0 | - | - | 5.0 |
| Citric acid | 1.0 | 1.0 | 1.0 | 1.0 |
| Na stannate | 0.0015 | 0.0015 | 0.0010 | 0.0015 |
| Na hydroxide | pH 4 | pH 4 | pH 4 | pH 4 |
| Water & minors | | | up to 100 % | |

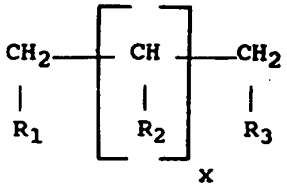
**Claims**

1. An aqueous bleaching composition comprising hydrogen peroxide and an organic peracid precursor, **characterized in** that the compositions have a pH in the range of from 3.5 to 6, and that the organic peracid precursor is a

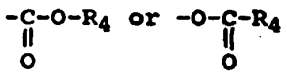


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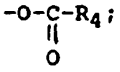
compound according to the formula:



wherein x is 0 or 1, $R_1$, $R_2$, $R_3$ are independently selected from -H, -OH,



where $R_4$ is $C_1$-$C_4$ alkyl, with the proviso that at least two of $R_1$, $R_2$ or $R_3$ are



or mixtures thereof.

2. A composition according to claim 1 which has a pH in the range of from 3.5 to 5.

3. A composition according to claim 2 which has a pH of about 4.

4. A composition according to any of the preceding claims wherein the organic peracid precursor is selected from ethylene glycol diesters, triacetin, diacetin, or mixtures thereof.

5. A composition according to claim 4 wherein the organic peracid precursor is selected from triacetin and ethylene glycol diacetate.

6. A composition according to any of the preceding claims which comprises from 0.5 % to 20 % by weight of the total composition of hydrogen peroxide.

7. A composition according to any of the preceding claims which comprises from 1 % to 15 % by weight of the total composition of said organic peracid precursor.

8. A composition according to claim 6 which comprises from 0.1 to 2 moles of said organic peracid precursor per mole of hydrogen peroxide.

9. A composition according to any of the preceding claims which comprises from 0.5 % to 15 % by weight of the total composition of a surfactant.

10. A composition according to any of the preceding claims which comprises citric acid.

11. A composition according to any of the preceding claims which comprises butylated hydroxy toluene.

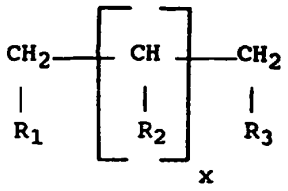
**Patentansprüche**

1. Wäßrige Bleichmittelzusammensetzung, umfassend Wasserstoffperoxid und einen organischen Persäurevorläu-

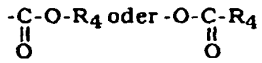


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fer, dadurch gekennzeichnet, daß die Zusammensetzung ein pH im Bereich von 3,5 bis 6 aufweist und daß der organische Persäurevorläufer eine Verbindung der Formel



ist, worin x 0 oder list, $R_1$, $R_2$, $R_3$ unabhängig voneinander aus -H, -OH,



gewählt sind, worin $R_4$ ein $C_1$-$C_4$-Alkyl ist, mit der Maßgabe, daß mindestens zwei von $R_1$, $R_2$ oder $R_3$



sind; oder Mischungen hiervon.

2. Zusammensetzung nach Anspruch 1, welche einen pH im Bereich von 3,5 bis 5 aufweist.

3. Zusammensetzung nach Anspruch 2, welche einen pH von etwa 4 aufweist.

4. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei der organische Persäurevorläufer aus Ethylenglycoldiestern, Triacetin. Diacetin oder Mischungen hiervon gewählt ist.

5. Zusammensetzung nach Anspruch 4, wobei der organische Persäurevorläufer aus Triacetin und Ethylenglycoldiacetat gewählt ist.

6. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 0,5 bis 20 Gew.-% der gesamten Zusammensetzung an Wasserstoffperoxid.

7. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 1-15 Gew.-% der gesamten Zusammensetzung des organischen Persäurevorläufers.

8. Zusammensetzung nach Anspruch 6, umfassend 0,1 bis 2 Mole des organischen Persäurevorläufers, pro Mol Wasserstoffperoxid.

9. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 0,5 bis 15 Gew.-% der gesamten Zusammensetzung eines Tensids.

10. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend Zitronensäure.

11. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend butyliertes Hydroxytoluol.

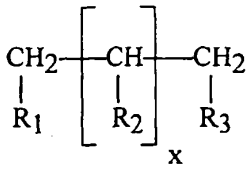
**Revendications**

1. Composition de blanchiment aqueuse comprenant du peroxyde d'hydrogène et un précurseur de peracide orga-

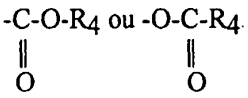


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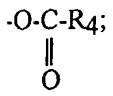
nique, caractérisée en ce que les compositions ont un pH dans le domaine de 3,5 à 6, et en ce que le précurseur de peracide organique est un composé répondant à la formule:



dans laquelle x vaut 0 ou 1, $R_1$, $R_2$, $R_3$ sont choisis indépendamment parmi -H, -OH,



où $R_4$ est un groupe alkyle en $C_1$-$C_4$, à condition qu'au moins deux des radicaux $R_1$, $R_2$ et $R_3$ soient



ou leurs mélanges.

2. Composition selon la revendication 1, qui possède un pH dans le domaine de 3,5 à 5.

3. Composition selon la revendication 2, qui possède un pH d'environ 4.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le précurseur de peracide organique est choisi parmi les diesters d'éthylèneglycol, la triacétine, la diacétine, ou leurs mélanges.

5. Composition selon la revendication 4, dans laquelle le précurseur de peracide organique est choisi parmi la triacétine et le diacétate d'éthylèneglycol.

6. Composition selon l'une quelconque des revendications précédentes, qui comprend de 0,5% à 20%, en poids de la composition totale, de peroxyde d'hydrogène.

7. Composition selon l'une quelconque des revendications précédentes, qui comprend de 1% à 15%, en poids de la composition totale, dudit précurseur de peracide organique.

8. Composition selon la revendication 6, qui comprend de 0,1 à 2 moles dudit précurseur de peracide organique par mole de peroxyde d'hydrogène.

9. Composition selon l'une quelconque des revendications précédentes, qui comprend de 0,5% à 15%, en poids de la composition totale, d'un tensioactif.

10. Composition selon l'une quelconque des revendications précédentes, qui comprend de l'acide citrique.

11. Composition selon l'une quelconque des revendications précédentes, qui comprend de l'hydroxytoluène butylé.



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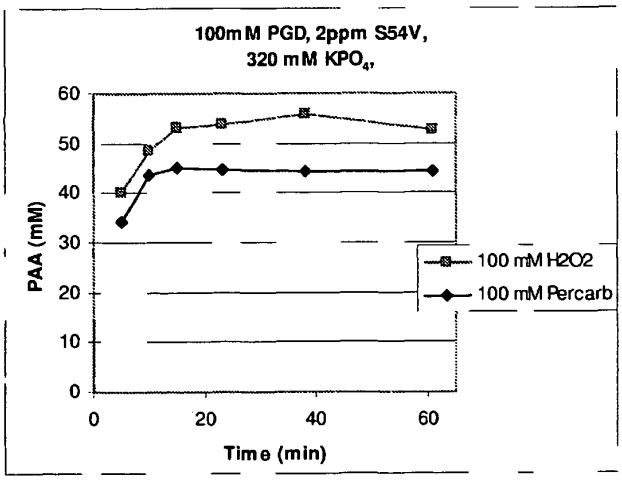



FIG. 1

(57) Abstract: The present invention provides stable compositions comprising a perhydrolase enzyme, a hydrogen peroxide source, and an ester substrate that efficiently generate aqueous peracid solutions. The generated peracid solutions are suitable for decontaminating and/or sanitizing a wide range of materials and equipment contaminated with pathogens or toxic chemicals. In one preferred embodiment, the stable composition comprises an acyl transferase enzyme, sodium percarbonate, and propylene glycol diacetate, and is stable for 30 days or longer. Upon addition to water, the composition is activated and generates an aqueous solution with a high ratio of peracetic acid to acetic acid.

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# STABLE ENZYMATIC PERACID GENERATING SYSTEMS

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[01]** This application claims the benefit of U.S. Provisional Application No. 60/917,252, filed on May 10, 2007, which is incorporated by reference herein in its entirety.

## FIELD OF THE INVENTION

**[02]** The present invention relates to stable compositions comprising a perhydrolase enzyme, a hydrogen peroxide source, and an ester substrate that efficiently generate aqueous peracid solutions suitable for use in decontamination involving a wide variety of chemical and biological warfare materials, as well as for general surface cleaning and decontamination.

## BACKGROUND OF THE INVENTION

**[03]** Peracids are widely accepted as a decontamination/disinfection agent. Most notably, peracetic acid (also known as "peroxyacetic acid" or "PAA") is employed widely, *inter alia,* for sterilization of items used in the food industry and in hospitals, as well as for decontamination of biohazards. PAA also can be used as a bleaching chemical in cleaning compositions and industrial processes such as bleaching of pulp. PAA poses relatively few disposal problems after use because it decomposes to compounds which are readily degraded in sewage treatment plants. It has a broad spectrum of activity against microorganisms, and is effective even at low temperatures.

**[04]** A number of non-enzymatic, chemical or electrochemical methods for preparing aqueous PAA solutions have been described in the prior art. See *e.g.,* U.S. Patent Nos. 6,677,477, 6,211,237, 6,171,551, 5,350,563, and 4,137,256, each of which is hereby incorporated by reference herein.

**[05]** The typical commercially available aqueous PAA solutions contain about 15% by weight PAA, about 14% by weight hydrogen peroxide, and 28% by weight acetic acid. The use of PAA solutions of this type causes, on account of their unpleasant corrosive and fire-accelerating properties, problems with regard to handling, storage, materials and transport. Thus, PAA has a large chemical "footprint" – meaning that safe production and use of this chemical requires an inordinate amount of energy and resources.

**[06]** Additionally, the higher ratio of acetic acid to PAA in these commercial solutions exacerbates problems related to the corrosion of stainless steel containers during the cleaning process. A lower ratio of acetic acid would reduce the need to further treat (*e.g.*, passivate) steel containers following cleaning with PAA.

**[07]** Some of these problems could be attenuated by the development of enzymatic systems for the *in situ* generation of peracids in aqueous solution. Enzymatic peracid generating systems provide numerous significant advantages due to the non-caustic characteristics of the water-based biochemical solvents, which allow users to safely use the system without fear of injury to themselves, their equipment, or the environment. In addition, there is a reduced logistical burden, as the enzyme systems are easily transported, easy to use, and require the use of much less water than traditional decontamination methods. Additionally, by-products of enzymatic peracid generating systems typically are biodegradable. For example, PAA decomposes spontaneously to acetic or propionic acid.

**[08]** PCT/US06/47022, filed December 8, 2006 (which is hereby incorporated by reference herein) discloses enzymes that efficiently generate aqueous peracid solution in sufficient quantity for use in a range of decontaminating and sanitizing applications. In some embodiments, PCT/US06/47022 discloses an acyl transferase enzyme from *Mycobacterium smegmatis* and variants that generate aqueous PAA solution when the enzyme is added to water along with percarbonate and propylene glycol diacetate (PGDA).

**[09]** Water soluble containers provide a convenient means for delivering pre-measured compositions into an aqueous solution. Such containers have been described for use with cleaning compositions in a number of U.S. patents. For example, U.S. Pat. No. 5,783,541 teaches a dishwashing composition disposed in a water soluble film, wherein the water soluble film is coated with a water dissolvable glue. U.S. Pat. No. 6,037,319, which teaches a water soluble sachet containing a cleaning composition containing an alcohol and hexylene glycol. U.S. Pat. No. 6,465,413 discloses laundering and dishwashing products contained in a water soluble film sachet, wherein the formulation comprises a granulated percarbonate compound mixed with and encapsulated in an encapsulating blend comprising sulfate, carboxy methyl cellulose and nonionic surfactant. U.S. Pat. No. 6,492,312 discloses a water soluble sachet comprising such a dishwashing composition along with a discrete particle that enhances cleaning in a dishwashing machine. US 20030199415 A1, teaches a cleaning system comprising a water soluble sachet containing a concentrate of a liquid



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cleaning composition having excellent foam collapse properties and excellent grease cutting property.

**[10]** U.S. Pat. No. 7,052,520 discloses a water-permeable, but not water-soluble, article referred to as a "sachet" or "bio-bag", for use in an enzymatic fabric cleaning. This "bio-bag" does not dissolve in water but rather contains the enzyme-producing micro-organisms in such a manner that they cannot disperse from it into the wash water.

**[11]** Notwithstanding the above developments in the art, there remains a need for an enzymatic system for generating peracids that exhibits greater stability, greater ease of use, while lessening the storage, transport and overall chemical issues created by the use of this class of compounds in commercial decontamination applications.

## SUMMARY OF THE INVENTION

**[12]** The present invention provides stable compositions, systems, and kits that enzymatically generate peracid in aqueous solution, and which can be used in a wide range of decontamination methods and applications.

**[13]** In some embodiments, the present invention provides stable compositions useful for generating peracid in aqueous solution, wherein said composition comprises: an enzyme with perhydrolase activity, a hydrogen peroxide source, and an ester substrate. These three active ingredients are activated by addition to water resulting in the generation of an aqueous peracid solution. It is a surprising result of the present invention that these compositions are highly stable prior to activation (*i.e.*, addition to water), wherein stability corresponds to the composition's ability to generate a peracid upon addition to water in an amount effective for use in sanitizing, disinfecting and/or decontaminating items. That is, the stable compositions of present invention retain their ability to generate peracid upon addition to water (*i.e.,* peracid generating activity) for at least 7 days, about 14 days, about 30 days, about 60 days, or longer.

**[14]** In some embodiments, the stable compositions include additional active ingredients such as additional enzymes, surfactants, detergent formulations, and/or cleaning compositions. However, in one preferred embodiment, the composition includes three active ingredients: an acyl transferase enzyme, the hydrogen peroxide source, and the ester substrate.

**[15]** In one preferred embodiment, the stable composition comprises the acyl transferase enzyme from *M. smegmatis* (MsAcT), sodium percarbonate, and propylene glycol diacetate (PGDA), wherein the enzyme and percarbonate are solids suspended in the liquid PGDA.



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In some embodiments, the perhydrolase enzyme comprises the amino acid sequence set forth in SEQ ID NO:1 or a variant or homologue thereof. In one embodiment, the perhydrolase enzyme is the S54V variant of SEQ ID NO:1.

**[16]** In one embodiment, the composition comprises from about 0.001% to about 1% by weight MsAcT, from about 35% to about 45% by weight sodium percarbonate, and from about 65% to about 55% by weight propylene glycol diacetate. Upon addition to water, the stable composition is activated and commences generating peracetic acid (PAA). The weight percent of PAA produced in water does not decrease significantly despite prior storage of the composition at ambient temperature for at least 7 days, about 14 days, about 30 days, about 60 days, or longer.

**[17]** In preferred embodiments, the resulting peracid aqueous solutions generated by the stable compositions are at least about 0.08%, 0.16%, 0.24%, 0.32%, 0.40%, or greater percentage by weight peracid. In embodiments of the stable composition that generate PAA, the resulting PAA aqueous solutions generated by the stable compositions are at least about 0.08%, 0.16%, 0.24%, 0.32%, 0.40%, or greater percentage by weight PAA. In one preferred embodiment, the PAA aqueous solution is at least about 0.16% PAA by weight.

**[18]** Additionally, the ratio of peracid to acid produced by the enzymatic activity of the stable composition added to water is at least about 2:1, 4:1, 5:1, 10:1, 20:1, or even greater. In embodiments of the stable composition that generate PAA, the ratio of PAA to acetic acid generated upon addition to water is at least about 2:1, 4:1, 5:1, 10:1, 20:1, or even greater.

**[19]** The present invention provides systems and kits for generating peracids in aqueous solution that based on the stable composition embodiments. Thus, in one embodiment the invention provides a system for generating peracetic acid in aqueous solution comprising any of the stable compositions of the present invention in a water soluble container. In some embodiments, the container is formed from a water soluble polymer, preferably a polyvinyl alcohol polymer. Generally, the water soluble container can be in any form, preferably a sachet, ampoule, capsule or sphere. In one preferred embodiment, the water soluble container is a sachet comprising a polyvinyl alcohol film.

**[20]** In another embodiment, the present invention provides a kit for decontamination comprising the packaged combination of: (a) a pre-measured amount of any of the stable compositions of the present invention in a sealed container, wherein the amount of the stable composition generates an aqueous solution of at least about 0.16% peracetic acid by weight upon addition to a set volume of water, and (b) instructions for use of the stable



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composition. In one embodiment, the sealed container of the kit is large enough to hold at least twice said set volume of water. In another embodiment, the kit further comprises the stable composition packaged within a water soluble container that is packaged within said sealed container. In one preferred embodiment, the water soluble container is a sachet made of a polyvinyl alcohol film. In an alternative embodiment, the packaged combination of the kit further comprises the set volume of water in a second sealed container, and wherein the water is sterilized.

**[21]** Generally, the stable compositions of the present invention, and the systems and kits incorporating the stable compositions, can be used in various methods for preparing aqueous solutions for decontaminating, disinfecting, and/or sanitizing items. Thus, the present invention also provides methods for preparing a decontamination solution comprising adding the stable composition useful for generating peracetic acid to water and mixing for at least about 30 minutes, 20 minutes, 15 minutes, 10 minutes, or even fewer minutes.

**[22]** In some embodiments, the method for decontamination comprises: (a) providing a stable composition comprising an enzyme with perhydrolase activity, wherein said activity comprises a perhydrolysis to hydrolysis ratio of at least 2:1; a hydrogen peroxide source; and an ester substrate; and (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about 0.16% peracetic acid by weight, and a pH less than about 9.0; and (c) exposing an item comprising a contaminant to said solution. In one embodiment, the solution of the stable composition includes no other ingredients capable of buffering the pH.

**[23]** In one preferred embodiment, the method for decontamination of the present invention comprises: (a) providing a stable composition comprising an acyl transferase enzyme, a hydrogen peroxide source, and propylene glycol diacetate; (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about 0.16% peracetic acid by weight; and (c) exposing an item comprising a contaminant to said solution. In some embodiments of the method for preparing a solution, the stable composition provided comprises from about 0.001% to about 1% by weight MsAcT, from about 35% to about 45% by weight sodium percarbonate, and from about 65% to about 55% by weight propylene glycol diacetate.

**[24]** In one preferred embodiment of the methods, the stable composition is contained in a water soluble container and the container is added to the water. In one preferred



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embodiment, the water soluble container is a sachet, ampoule, capsule or sphere, formed from a water soluble polymer, preferably a polyvinyl alcohol polymer.

**[25]** In various embodiments, the methods of the invention are useful against a wide range of contaminants including toxins selected from the group consisting of botulinum toxin, anthracis toxin, ricin, scombroid toxin, ciguatoxin, tetrodotoxin, mycotoxins, and any combination thereof; and pathogens selected from the group consisting of bacteria, viruses, fungi, parasites, prions, and any combination thereof. In one embodiment, the methods of the invention are useful against biofilms, including those formed by pathogens including but not limited to: *Pseudomonas aeruginosa*, *Staphylococcus aureus* (SRWC-10943), and *Listeria monocytogenes* (ATCC 19112).

**[26]** In various embodiments, the methods of the invention are useful for decontaminating and/or sanitizing a wide range of contaminated items including hard surfaces, fabrics, food, feed, apparel, rugs, carpets, textiles, medical instruments, veterinary instruments, pharmaceutical processing equipment, and biotechnology processing equipment. In one preferred embodiment, PAA solutions generated using the stable compositions of the present invention may be used to sanitize stainless steel equipment, including large reactors, used in pharmaceutical and biotechnology processes.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[27]** Figure 1 provides a graph showing the enzymatic generation of PAA from hydrogen peroxide or percarbonate.

**[28]** Figure 2 provides a graph showing the generation of PAA from glucose and propyleneglycol diacetate.

**[29]** Figure 3 provides a graph showing the generation of PAA at three different temperatures (21°C, 40°C, and 60°C).

**[30]** Figure 4 provides a graph showing the ability of the acetyl transferase enzyme to produce concentrated PAA.

## DETAILED DESCRIPTION OF THE INVENTION

### I. Overview

**[31]** The present invention provides stable compositions, systems, kits, that enzymatically generate peracids in aqueous solution, and which can be used in a wide range of decontamination methods and applications. The present invention is based in part on the surprising discovery that compositions comprising a perhydrolase enzyme, such as acyl transferase, a hydrogen peroxide source, and an ester substrate, such as propylene



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glycol diacetate, are extremely stable prior to use. Indeed, compositions of these three components can be stable for at least 7 days, about 14 days, about 30 days, about 60 days, or longer, wherein stability corresponds to the ability to generate an effective amount of peracid upon addition to water.

**[32]** Peracids (*e.g.*, peracetic acid) are well-characterized decontamination agents that are accepted and approved for use in a wide range of applications. *In-situ* enzymatic peracetic acid generation in water, which occurs with a preferred embodiment of the stable composition, systems and kits of the present invention, is desirable as it is much safer than reactive chemical generation in solvents and requires much less volume. Thus, the present invention provides a stable composition that is convenient, simple to use, and highly effective for a wide range decontamination methods and techniques. For example, the stable compositions of the present invention may be used in decontaminating chemical and biological warfare materials, as well as for general surface cleaning and decontamination

**[33]** In one preferred embodiment, the stable composition comprises the acyl transferase enzyme, MsAcT from *M. smegmatis*, and sodium percarbonate as hydrogen peroxide source. In one embodiment, the composition comprises from about 0.001% to about 1% by weight MsAcT, from about 35% to about 45% by weight sodium percarbonate, and from about 65% to about 55% by weight propylene glycol diacetate.

**[34]** The stable composition of the present provides numerous advantages over currently used methods that utilize peracid for cleaning, disinfection and/or decontamination. Significantly, the composition is a stable "All-In-One" composition, wherein all of the ingredients are formulated together (*e.g.*, in a single container or package). Consequently, usage of the composition only requires adding the contents of a single container to water. Additionally, the present invention also provides the stable composition in a sealed water soluble container, which allows the further convenience of not having to even open a container. Instead, the composition in the water soluble container is added to water, thereby providing an aqueous solution convenient for decontamination use.

## II. Definitions

**[35]** Unless defined otherwise herein, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention pertains. For example, Singleton and Sainsbury, *Dictionary of Microbiology and*



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*Molecular Biology*, 2d Ed., John Wiley and Sons, NY (1994); and Hale and Marham, *The Harper Collins Dictionary of Biology*, Harper Perennial, NY (1991) provide those of skill in the art with a general dictionaries of many of the terms used in the invention. Although any methods and materials similar or equivalent to those described herein find use in the practice of the present invention, the preferred methods and materials are described herein. Accordingly, the terms defined immediately below are more fully described by reference to the Specification as a whole. Also, as used herein, the singular terms "a," "an," and "the" include the plural reference unless the context clearly indicates otherwise. Unless otherwise indicated, nucleic acids are written left to right in 5' to 3' orientation; amino acid sequences are written left to right in amino to carboxy orientation, respectively. It is to be understood that this invention is not limited to the particular methodology, protocols, and reagents described, as these may vary, depending upon the context in which they are used by those of skill in the art.

**[36]** It is intended that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

**[37]** As used herein, the term "enzyme" refers to any protein that catalyzes a chemical reaction. The catalytic function of an enzyme constitutes its "activity" or "enzymatic activity." An enzyme typically is classified according to the type of catalytic function it carries out, *e.g.*, hydrolysis of peptide bonds.

**[38]** As used herein, the term "substrate" refers to a substance (*e.g.*, a chemical compound) on which an enzyme performs its catalytic activity to generate a product.

**[39]** A "perhydrolase" refers to an enzyme that is capable of catalyzing a perhydrolysis reaction that results in the production of a sufficiently high amount of peracid suitable for use in an application such as cleaning, bleaching, disinfection, or sterilization. Generally, a perhydrolase enzyme used in methods described herein exhibits a high perhydrolysis to hydrolysis ratio. In some embodiments, the perhydrolase comprises, consists of, or consists essentially of the *Mycobacterium smegmatis* perhydrolase amino acid sequence set forth in



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SEQ ID NO:1, or a variant or homolog thereof. In some embodiments, the perhydrolase enzyme comprises acyl transferase activity and catalyzes an aqueous acyl transfer reaction.

**[40]** A "peracid" is an organic acid of the formula RC(=O)OOH.

**[41]** "Perhydrolysis" or "perhydrolyze" refers to an enzymatic reaction that produces a peracid. In some embodiments, a peracid is produced by perhydrolysis of an ester substrate of the formula $R_1C(=O)OR_2$, where $R_1$ and $R_2$ are the same or different organic moieties, in the presence of hydrogen peroxide ($H_2O_2$).

**[42]** The phrase "source of hydrogen peroxide" includes hydrogen peroxide as well as the components of a system that can spontaneously or enzymatically produce hydrogen peroxide as a reaction product.

**[43]** The phrase "perhydrolysis to hydrolysis ratio" refers to the ratio of the amount of enzymatically produced peracid to the amount of enzymatically produced acid by a perhydrolase enzyme from an ester substrate under defined conditions and within a defined time.

**[44]** As used herein, the term "acyl" refers to an organic acid group, which is the residue of a carboxylic acid after removal of a hydroxyl (-OH) group (*e.g.*, ethanoyl chloride, $CH_3CO$-Cl, is the acyl chloride formed from ethanoic acid, $CH_3CO$-OH). The name of an individual acyl group is general formed by replacing the "-ic" of the acid by "-yl."

**[45]** As used herein, the term "acylation" refers to a chemical transformation in which an acyl (RCO-) group is substituted into a molecule, generally for an active hydrogen of an -OH group.

**[46]** As used herein, the term "transferase" refers to an enzyme that catalyzes the transfer of a functional group from one substrate to another substrate.

**[47]** As used herein, the term "enzymatic conversion" refers to the modification of a substrate or intermediate to a product, by contacting the substrate or intermediate with an enzyme. In some embodiments, contact is made by directly exposing the substrate or intermediate to the appropriate enzyme. In other embodiments, contacting comprises exposing the substrate or intermediate to an organism that expresses and/or excretes the enzyme, and/or metabolizes the desired substrate and/or intermediate to the desired intermediate and/or end-product, respectively.

**[48]** As used herein, "effective amount of enzyme" refers to the quantity of enzyme necessary to achieve the activity required in the specific application (*e.g.*, production of peracetic acid by acyl transferase for use in decontamination). Such effective amounts are readily ascertained by one of ordinary skill in the art and are based on many factors, such as



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the particular enzyme variant used, the specific composition, the method of decontamination, the item to be decontaminated, and the like.

**[49]** As used herein, the term "stability" in reference to a substance (*e.g.*, an enzyme) or composition refers to its ability to maintain a certain level of functional activity over a period of time under certain environmental conditions. Furthermore, the term "stability" can be used in a number of more specific contexts referring to the particular environmental condition that is of interest. For example, "thermal stability" as used herein refers to the ability of a substance or composition to maintain its function (*i.e.*, not degrade) at increased temperature. A substantial change in stability is evidenced by at least about a 5% or greater increase or decrease (in most embodiments, it is preferably an increase) in the half-life of the functional activity being assayed, as compared to the activity present in the absence of the selected environmental conditions.

**[50]** As used herein, the term "chemical stability" as used in reference to an enzyme refers to the stability of the enzyme in the presence of chemicals that adversely affect its activity. In some embodiments, such chemicals include, but are not limited to hydrogen peroxide, peracids, anionic detergents, cationic detergents, non-ionic detergents, chelants, etc. However, it is not intended that the present invention be limited to any particular chemical stability level nor range of chemical stability.

**[51]** As used herein, "pH stability" refers to the ability of a substance (*e.g.*, an enzyme) or composition to function at a particular pH. Stability at various pHs can be measured either by standard procedures known to those in the art and/or by the methods described herein. A substantial change in pH stability is evidenced by at least about 5% or greater increase or decrease (in most embodiments, it is preferably an increase) in the half-life of the functional activity, as compared to the activity at the optimum pH. It is not intended that the present invention be limited to any pH stability level nor pH range.

**[52]** As used herein, "oxidative stability" refers to the ability of a substance (*e.g.*, an enzyme) or composition to function under oxidative conditions, *e.g.*, in the presence of an oxidizing chemical.

**[53]** As used herein, "oxidizing chemical" refers to a chemical that has the capability of bleaching. The oxidizing chemical is present at an amount, pH and temperature suitable for bleaching. The term includes, but is not limited to hydrogen peroxide and peracids.

**[54]** As used herein, the terms "purified" and "isolated" refer to the removal of contaminants from a sample. For example, an acyl transferase is purified by removal of



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contaminating proteins and other compounds within a solution or preparation that are not acyl transferases.

**[55]** As used herein, the term "contaminant" refers to any substance which by its contact or association with another substance, material, or item makes it undesirable, impure, and/or unfit for use.

**[56]** As used herein, the term "a contaminated item" or "item in need of decontamination" refers to any item or thing in contact or associated with a contaminant and/or which needs to be decontaminated. It is not intended that the item be limited to any particular thing or type of item. For example, in some embodiments, the item is a hard surface, while in other embodiments, the item is an article of clothing. In yet additional embodiments, the item is a textile. In yet further embodiments, the item is used in the medical and/or veterinary fields. In some preferred embodiments, the item is a surgical instrument. In further embodiments, the item is used in transportation (*e.g.*, roads, runways, railways, trains, cars, planes, ships, etc.). In further embodiments, the term is used in reference to food and/or feedstuffs, including but not limited to meat, meat by-products, fish, seafood, vegetables, fruits, dairy products, grains, baking products, silage, hays, forage, etc. Indeed, it is intended that the term encompass any item that is suitable for decontamination using the methods and compositions provided herein.

**[57]** As used herein, the term "decontamination" refers to the removal of substantially all or all contaminants from a contaminated item. In some preferred embodiments, decontamination encompasses disinfection, while in other embodiments, the term encompasses sterilization. However, it is not intended that the term be limited to these embodiments, as the term is intended to encompass the removal of inanimate contaminants, as well as microbial contamination. (*e.g.*, bacterial, fungal, viral, prions, etc.).

**[58]** As used herein, the term "disinfecting" refers to the removal of contaminants from the surfaces, as well as the inhibition or killing of microbes on the surfaces of items. It is not intended that the present invention be limited to any particular surface, item, or contaminant(s) or microbes to be removed.

**[59]** As used herein, the term "sterilizing" refers to the killing of all microbial organisms on a surface.

**[60]** As used herein, the term "sporicidal" refers to the killing of microbial spores, including but not limited to fungal and bacterial spores. The term encompasses compositions that are effective in preventing germination of spores, as well as those compositions that render spores completely non-viable.



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**[61]** As used herein, the terms "bactericidal," "fungicidal," and "viricidal" refer to compositions that kill bacteria, fungi, and viruses, respectively. The term "microbiocidal" refers to compositions that inhibit the growth and/or replication of any microorganisms, including but not limited to bacteria, fungi, viruses, protozoa, rickettsia, etc.

**[62]** As used herein, the terms "bacteriostatic," "fungistatic," and "virostatic" refer to compositions that inhibit the growth and/or replication of bacteria, fungi, and viruses, respectively. The term "microbiostatic" refers to compositions that inhibit the growth and/or replication of any microorganisms, including but not limited to bacteria, fungi, viruses, protozoa, rickettsia, etc.

**[63]** As used herein, the term "cleaning composition" refers to compositions that find use in the removal of undesired compounds from items to be cleaned, such as fabric, dishes, contact lenses, other solid substrates, hair (shampoos), skin (soaps and creams), teeth (mouthwashes, toothpastes) etc. The term further refers to any composition that is suited for cleaning, bleaching, disinfecting, and/or sterilizing any object and/or surface. It is intended that the term includes, but is not limited to detergent compositions (*e.g.*, liquid and/or solid laundry detergents and fine fabric detergents; hard surface cleaning formulations, such as for glass, wood, ceramic and metal counter tops and windows; carpet cleaners; oven cleaners; fabric fresheners; fabric softeners; and textile and laundry pre-spotters, as well as dish detergents). The term further encompasses any materials/compounds selected for the particular type of cleaning composition desired and the form of the product (*e.g.*, liquid, gel, granule, or spray composition), as long as the composition is compatible with the acyl transferase, hydrogen peroxide source, PGDA, and any other enzyme(s) or substance used in the composition. The specific selection of cleaning composition materials is readily made by considering the surface, item or fabric to be cleaned, and the desired form of the composition for the cleaning conditions during use. Indeed, the term "cleaning composition" as used herein, includes unless otherwise indicated, granular or powder-form all-purpose or heavy-duty washing agents, especially cleaning detergents; liquid, gel or paste-form all-purpose washing agents, especially the so-called heavy-duty liquid (HDL) types; liquid fine-fabric detergents; hand dishwashing agents or light duty dishwashing agents, especially those of the high-foaming type; machine dishwashing agents, including the various tablet, granular, liquid and rinse-aid types for household and institutional use; liquid cleaning and disinfecting agents, including antibacterial hand-wash types, cleaning bars, mouthwashes, denture cleaners, car or carpet shampoos, bathroom cleaners; hair shampoos and hair-rinses; shower gels and foam baths



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and metal cleaners; as well as cleaning auxiliaries such as bleach additives and "stain-stick" or pre-treat types.

**[64]** As used herein, the terms "detergent composition" and "detergent formulation" are used in reference to mixtures which are intended for use in a wash medium for the cleaning of soiled objects. In some preferred embodiments, the term is used in reference to laundering fabrics and/or garments (*e.g.*, "laundry detergents"). In alternative embodiments, the term refers to other detergents, such as those used to clean dishes, cutlery, etc. (*e.g.*, "dishwashing detergents"). It is not intended that the present invention be limited to any particular detergent formulation or composition. Indeed, it is intended that in addition to a perhydrolase enzyme, *e.g.*, an acyl transferase, the term encompasses detergents that contain surfactants, transferase(s), hydrolytic enzymes, oxido reductases, builders, bleaching agents, bleach activators, bluing agents and fluorescent dyes, caking inhibitors, masking agents, enzyme activators, antioxidants, and solubilizers.

**[65]** As used herein, the term "enzyme compatible," when used in the context of cleaning composition materials means that the materials do not reduce the enzymatic activity to such an extent that the relevant enzyme is not effective as desired during normal use situations.

**[66]** As used herein, "protein" refers to any composition comprised of amino acids and recognized as a protein by those of skill in the art. The terms "protein," "peptide" and polypeptide are used interchangeably herein. Wherein a peptide is a portion of a protein, those skilled in the art understand the use of the term in context. The terms "wild-type" and "native" are used to refer to proteins found in nature. In some embodiments, the wild-type protein's sequence is the starting point of a protein engineering project.

**[67]** As used herein, the terms "related protein" or "homologous protein" refer to proteins that are functionally and/or structurally similar (*i.e.*, have similar action and/or structure). It is intended that the term encompass the same or similar enzyme(s) (*i.e.*, in terms of structure and function) obtained from different species. It is not intended that the present invention be limited to related proteins from any particular source(s) or proteins related evolutionarily. In addition, the term related or homologous proteins encompasses tertiary structural homologs and primary sequence homologs. Thus, the terms include proteins with "variant" or "mutant" sequences relative to the wild-type sequence.

**[68]** As used herein, the term "derivative" refers to a protein which is derived from a parent protein by addition of one or more amino acids to either or both of the C- and N-terminal end(s), substitution of one or more amino acids at one or a number of different sites in the amino acid sequence, and/or deletion of one or more amino acids at either or



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both C- and N- terminal end(s) and/or at one or more sites in the amino acid sequence, and/or insertion of one or more amino acids at one or more sites in the amino acid sequence. The preparation of a protein derivative is often achieved by modifying a DNA sequence that encodes a native protein, transformation of the modified DNA sequence into a suitable host, and expression of the modified DNA sequence to produce the derivative protein.

**[69]** Related (and derivative) proteins encompass "variant" proteins. Variant proteins differ from a parent protein and/or from one another by a small number of amino acid residues. In some embodiments, the number of different amino acid residues is any of about 1, 2, 3, 4, 5, 10, 20, 25, 30, 35, 40, 45, or 50. In some embodiments, variants differ by about 1 to about 10 amino acids.

**[70]** In some embodiments, related proteins, such as variant proteins, comprise any of at least about 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, 97%, 98%, 99%, or 99.5% amino acid sequence identity.

**[71]** As used herein, the term "analogous sequence" refers to a polypeptide sequence within a protein that provides a similar function, tertiary structure, and/or conserved residues with respect to a reference protein. For example, in epitope regions that contain an alpha helix or a beta sheet structure, replacement amino acid(s) in an analogous sequence maintain the same structural element. In some embodiments, analogous sequences are provided that result in a variant enzyme exhibiting a similar or improved function with respect to the parent protein from which the variant is derived.

**[72]** As used herein, "homologous protein" refers to a protein (*e.g.*, a perhydrolase enzyme) that has similar function (*e.g.*, enzymatic activity) and/or structure as a reference protein (*e.g.*, a perhydrolase enzyme from a different source). Homologs may be from evolutionarily related or unrelated species. In some embodiments, a homolog has a quaternary, tertiary and/or primary structure similar to that of a reference protein, thereby potentially allowing for replacement of a segment or fragment in the reference protein with an analogous segment or fragment from the homolog, with reduced disruptiveness of structure and/or function of the reference protein in comparison with replacement of the segment or fragment with a sequence from a non-homologous protein.

**[73]** As used herein, "wild-type," "native," and "naturally-occurring" proteins are those found in nature. The terms "wild-type sequence" refers to an amino acid or nucleic acid sequence that is found in nature or naturally occurring. In some embodiments, a wild-type sequence is the starting point of a protein engineering project, for example, production of variant proteins.



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### III. Enzymatic Generation of Peracid in Aqueous Solution

**[74]** The stable compositions of the present invention comprise at least one enzyme as a component (*i.e.*, ingredient). Generally, the enzymes used in the present invention must have significant perhydrolase activity – *i.e.*, a catalytic activity that results in the formation of high amounts of peracid suitable for applications such as cleaning, bleaching, and disinfecting. The use of enzymes with perhydrolase activity for peracid generation is described in WO 05/056782, which is hereby incorporated by reference herein in its entirety.

**[75]** Typically, enzymatic perhydrolase activity is accompanied by hydrolase activity. Indeed, as discussed below, many hydrolase enzymes also act as perhydrolases in the presence of hydrogen peroxide. In particularly preferred embodiments, the enzymes of the present invention have very high ratio of perhydrolase to hydrolase activity, and thereby produce a high ratio of peracid relative to acid products (*e.g.*, ratio of peracid to acid of at least about 2:1, 5:1, 10:1, or greater). These high perhydrolysis to hydrolysis ratios of these distinct enzymes makes these enzymes suitable for use in a very wide variety of applications.

**[76]** In addition to having significant perhydrolase activity, the enzymes useful in the stable compositions of the present invention exhibit relatively low activity in dry or substantially water free conditions. In some embodiments, the enzyme component of the stable composition has less than about 1%, 0.5%, 0.2%, or less than about 0.1% activity (perhydrolase or hydrolase) when there is less about 1% water by weight present in the composition. In preferred embodiments, the enzyme exhibits less than about 0.1% activity when there is about 2% water by weight present or less.

**[77]** In some embodiments, the perhydrolase enzyme is naturally-occurring (*i.e.*, a perhydrolase enzyme encoded by a genome of a cell). In some embodiments, the perhydrolase enzyme comprises, consists of, or consists essentially of an amino acid sequence that is at least about 80%, 85%, 90%, 95%, 97%, 98%, 99%, or 99.5% identical to the amino acid sequence of a naturally-occurring perhydrolase enzyme.

**[78]** In some embodiments, the perhydrolase enzyme has a perhydrolysis:hydrolysis ratio of at least 1.



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*1. Acyl transferase enzymes – MsAcT from M. smegmatis*

**[79]** In one embodiment, the present invention provides a stable composition comprising an acyl transferase capable of the enzymatic conversion of hydrogen peroxide and ester substrate to peracid in aqueous solution. In preferred embodiments, the stable compositions of the present invention use acyl transferase enzymes that produce very high perhydrolysis to hydrolysis ratios. High perhydrolysis to hydrolysis ratios means that these enzymes produce higher yields of peracid, making them more effective in generating decontamination solutions.

**[80]** An acyl transferase with a favorable perhydrolysis to hydrolysis ratio that makes it particularly well-suited for the present invention is the *M. smegmatis* acyl transferase (MsAcT). For example, MsAcT when used to enzymatically convert PGDA and hydrogen peroxide from percarbonate generates PAA product in at least 5:1 excess over acetic acid. Because the MsAcT produces a high ratio of PAA to acetic acid, the pH of the resulting aqueous peracid solution is able to remain at relatively low pH, less than about pH 10, about pH 9.0, about pH 8.5, about pH 8.0, or about pH 7.5. Such low pH PAA (or other peracid) aqueous solutions are considered non-corrosive (or at least substantially less corrosive) to metals than typical commercial PAA solutions which contain high levels of acetic acid.

**[81]** Additionally, the MsAcT is essentially inactive in the absence of water. The MsAcT enzyme requires a significant amount of water present (*i.e.*, relatively high degree of hydration) in order to exhibit perhydrolase or hydrolase activity. Typically, MsAcT and it variants exhibit less than about 1%, 0.5%, 0.2%, or less than about 0.1% activity (perhydrolase or hydrolases) when there is less about 1% water by weight present in the composition that includes the enzyme.

**[82]** The wild-type *M. smegmatis* acyl transferase is described in WO 05/056782, which is hereby incorporated by reference herein in its entirety. PCT/US06/47022, filed December 8, 2006, which also is incorporated by reference herein, discloses a number of MsAcT variants including S54V-MsAcT, and the use of the wild-type and variants to generate aqueous peracid solution when the enzyme is added to water along with a hydrogen peroxide source and an ester substrate (*e.g.*, propylene glycol diacetate (PGDA)).

**[83]** In some embodiments, the perhydrolase enzyme is a naturally occurring *M. smegmatis* perhydrolase enzyme. In some embodiments, a perhydrolase enzyme comprises, consists of, or consists essentially of the amino acid sequence set forth in SEQ ID NO:1 or a variant or homologue thereof. In some embodiments, a perhydrolase enzyme comprises, consists of, or consists essentially of an amino acid sequence that is at least about 80%,



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85%, 90%, 95%, 97%, 98%, 99%, or 99.5% identical to the amino acid sequence set forth in SEQ ID NO:1.

**[84]** The amino acid sequence of *M. smegmatis* perhydrolase is shown below:

MAKRILCFGDSLTWGWVPVEDGAPTERFAPDVRWTGVLAQQLGADFEVIEEGLSA
RTTNIDDPTDPRLNGASYLPSCLATHLPLDLVIIMLGTNDTKAYFRRTPLDIALGMS
VLVTQVLTSAGGVGTTYPAPKVLVVSPPPLAPMPHPWFQLIFEGGEQKTTELARVY
SALASFMKVPFFDAGSVISTDGVDGIHFTEANNRDLGVALAEQVRSLL (SEQ ID NO:1)

**[85]** The corresponding polynucleotide sequence encoding *M. smegmatis* perhydrolase is:

5'-ATGGCCAAGCGAATTCTGTGTTTCGGTGATTCCCTGACCTGGGGCTGGGTCC
CCGTCGAAGACGGGGCACCCACCGAGCGGTTCGCCCCCGACGTGCGCTGGACC
GGTGTGCTGGCCCAGCAGCTCGGAGCGGACTTCGAGGTGATCGAGGAGGGACT
GAGCGCGCGCACCACCAACATCGACGACCCCACCGATCCGCGGCTCAACGGCG
CGAGCTACCTGCCGTCGTGCCTCGCGACGCACCTGCCGCTCGACCTGGTGATCA
TCATGCTGGGCACCAACGACACCAAGGCCTACTTCCGGCGCACCCCGCTCGACA
TCGCGCTGGGCATGTCGGTGCTCGTCACGCAGGTGCTCACCAGCGCGGGCGGCG
TCGGCACCACGTACCCGGCACCCAAGGTGCTGGTGGTCTCGCCGCCACCGCTGG
CGCCCATGCCGCACCCCTGGTTCCAGTTGATCTTCGAGGGCGGCGAGCAGAAGA
CCACTGAGCTCGCCCGCGTGTACAGCGCGCTCGCGTCGTTCATGAAGGTGCCGT
TCTTCGACGCGGGTTCGGTGATCAGCACCGACGGCGTCGACGGAATCCACTTCA
CCGAGGCCAACAATCGCGATCTCGGGGTGGCCCTCGCGGAACAGGTGCGGAGC
CTGCTGTAA-3' (SEQ ID NO:2)

*2. Variant Acyl Transferase Enzymes*

**[86]** It is not intended that the stable compositions of the present invention be limited to including wild type *M. smegmatis* acyl transferase. In alternative embodiments, an acyl transferase can be used that is a homolog or engineered variant of the MsAcT acyl transferase. In further preferred embodiments, a monomeric hydrolase is engineered to produce a monomeric or multimeric enzyme that has better acyl transferase activity than the native monomeric enzyme. In some particularly preferred embodiments, the variant comprises the substitution S54V of MsAcT (referred to herein as "S54V-MsAcT" or the "S54V variant" or "variant S54V").

**[87]** In other embodiments, the acyl transferase used in the stable composition is one of the variant enzymes or homologs disclosed and described in WO 05/056782.



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**[88]** In some embodiments, the perhydrolase enzyme comprises one or more substitutions at one or more amino acid positions equivalent to position(s) in the *M. smegmatis* perhydrolase amino acid sequence set forth in SEQ ID NO:1. In some embodiments, the perhydrolase enzyme comprises any one or any combination of substitutions of amino acids selected from M1, K3, R4, I5, L6, C7, D10, S11, L12, T13, W14, W16, G15, V17, P18, V19, D21, G22, A23, P24, T25, E26, R27, F28, A29, P30, D31, V32, R33, W34, T35, G36, L38, Q40, Q41, D45, L42, G43, A44, F46, E47, V48, I49, E50, E51, G52, L53, S54, A55, R56, T57, T58, N59, I60, D61, D62, P63, T64, D65, P66, R67, L68, N69, G70, A71, S72, Y73, S76, C77, L78, A79, T80, L82, P83, L84, D85, L86, V87, N94, D95, T96, K97, Y99F100, R101, R102, P104, L105, D106, I107, A108, L109, G110, M111, S112, V113, L114, V115, T116, Q117, V118, L119, T120, S121, A122, G124, V125, G126, T127, T128, Y129, P146, P148, W149, F150, I153, F154, I194, and F196.

**[89]** In some embodiments, the perhydrolase enzyme comprises one or more of the following substitutions at one or more amino acid positions equivalent to position(s) in the *M. smegmatis* perhydrolase amino acid sequence set forth in SEQ ID NO:1: L12C, Q, or G; T25S, G, or P; L53H, Q, G, or S; S54V, L A, P, T, or R; A55G or T; R67T, Q, N, G, E, L, or F; K97R; V125S, G, R, A, or P; F154Y; F196G.

**[90]** In some embodiments, the perhydrolase enzyme comprises a combination of amino acid substitutions at amino acid positions equivalent to amino acid positions in the *M. smegmatis* perhydrolase amino acid sequence set forth in SEQ ID NO:1: L12I S54V; L12M S54T; L12T S54V; L12Q T25S S54V; L53H S54V; S54P V125R; S54V V125G; S54V F196G; S54V K97R V125G; or A55G R67T K97R V125G.

**[91]** Several methods are known in the art that are suitable for generating variants of the acyl transferase enzymes of the present invention, including but not limited to site-saturation mutagenesis, scanning mutagenesis, insertional mutagenesis, random mutagenesis, site-directed mutagenesis, and directed-evolution, as well as various other recombinatorial approaches.

**[92]** In some embodiments, acyl transferases useful with the present invention include engineered variants within the SGNH-hydrolase family of proteins. In some preferred embodiments, the engineered proteins comprise at least one or a combination of the following conserved residues: L6, W14, W34, L38, R56, D62, L74, L78, H81, P83, M90, K97, G110, L114, L135, F180, G205. In alternative embodiments, these engineered proteins comprise the GDSL-GRTT and/or ARTT motifs. In further embodiments, the



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enzymes are multimers, including but not limited to dimers, octamers, and tetramers. In yet additional preferred embodiments, the engineered proteins exhibit a perhydrolysis to hydrolysis ratio that is greater than about 1:1, 2:1, 5:1, or even 10:1.

**[93]** An amino acid residue of an acyl transferase is equivalent to a residue of *M. smegmatis* acyl transferase if it is either homologous (*i.e.*, having a corresponding position in either the primary and/or tertiary structure) or analogous to a specific residue or portion of that residue in *M. smegmatis* acyl transferase (*i.e.*, having the same or similar functional capacity to combine, react, and/or chemically interact).

**[94]** In some embodiments, in order to establish homology to primary structure, the amino acid sequence of an acyl transferase is directly compared to the *M. smegmatis* acyl transferase primary sequence and particularly to a set of residues known to be invariant in all acyl transferases for which sequence is known. After aligning the conserved residues, allowing for necessary insertions and deletions in order to maintain alignment (*i.e.*, avoiding the elimination of conserved residues through arbitrary deletion and insertion), the residues equivalent to particular amino acids in the primary sequence of *M. smegmatis* acyl transferase are defined. In preferred embodiments, alignment of conserved residues conserves 100% of such residues. However, alignment of greater than 75% or as little as 50% of conserved residues is also adequate to define equivalent residues. In preferred embodiments, conservation of the catalytic serine and histidine residues are maintained.

**[95]** Conserved residues are used to define the corresponding equivalent amino acid residues of *M. smegmatis* acyl transferase in other acyl transferases (*e.g.*, acyl transferases from other *Mycobacterium* species, as well as any other organisms).

**[96]** In some embodiments, the following residues of *M. smegmatis* acyl transferase are modified: Cys7, Asp10, Ser11, Leu12, Thr13, Trp14, Trp16, Pro24, Thr25, Leu53, Ser54, Ala55, Thr64, Asp65, Arg67, Cys77, Thr91, Asn94, Asp95, Tyr99, Val125, Pro138, Leu140, Pro146, Pro148, Trp149, Phe150, Ile153, Phe154, Thr159, Thr186, Ile192, Ile194, and Phe196. However, it is not intended that the present invention be limited to sequence that are modified at these positions. Indeed, it is intended that the present invention encompass various modifications and combinations of modifications.

**[97]** In some embodiments, some of the residues identified for substitution, insertion or deletion are conserved residues whereas others are not. The acyl transferase mutants of the present invention include various mutants, including those encoded by nucleic acid that comprises a signal sequence. In some embodiments of acyl transferase mutants that are



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encoded by such a sequence are secreted by an expression host. In some further embodiments, the nucleic acid sequence comprises a homolog having a secretion signal.

**[98]** Characterization of wild-type and mutant proteins is accomplished via any means suitable and is preferably based on the assessment of properties of interest. For example, pH and/or temperature, as well as detergent and /or oxidative stability is/are determined in some embodiments of the present invention. Indeed, it is contemplated that enzymes having various degrees of stability in one or more of these characteristics (pH, temperature, proteolytic stability, detergent stability, and/or oxidative stability) will find use. In still other embodiments, acyl transferases with low peracid degradation activity are selected.

*3. Other Enzymes*

**[99]** Although acyl transferase from *M. smegmatis* (MsAcT) is used in one preferred embodiment of the stable compositions, any perhydrolase enzyme obtained from any source which in the presence of hydrogen peroxide converts an ester substrate into mostly peracid may be used in the present invention. In preferred embodiments, the enzyme exhibit a perhydrolysis to hydrolysis ratio that is greater than about 2:1, 5:1, or even 10:1. Consequently, the ratio of peracid to acid product is greater than about 2:1, 5:1, or even 10:1, and the pH of the resulting aqueous peracid solution is able to remain relatively low, *e.g.*, less than about pH 10, about pH 9.0, about pH 8.5, about pH 8.0, or about pH 7.5.

**[100]** In addition to the acyl transferase enzymes, various hydrolases have perhydrolase activity that makes them useful as enzymes in the compositions of the present invention. Thus, hydrolases useful in the present invention include but are not limited to: carboxylate ester hydrolase, thioester hydrolase, phosphate monoester hydrolase, and phosphate diester hydrolase which act on ester bonds; a thioether hydrolase which acts on ether bonds; and α-amino-acyl-peptide hydrolase, peptidyl-amino acid hydrolase, acyl-amino acid hydrolase, dipeptide hydrolase, and peptidyl-peptide hydrolase which act on peptide bonds. Such hydrolase(s) find use alone or in combination with MsAcT or another perhydrolase. Preferable among them are carboxylate ester hydrolase, and peptidyl-peptide hydrolase.

**[101]** Other suitable hydrolases include: (1) proteases belonging to the peptidyl-peptide hydrolase class (*e.g.*, pepsin, pepsin B, rennin, trypsin, chymotrypsin A, chymotrypsin B, elastase, enterokinase, cathepsin C, papain, chymopapain, ficin, thrombin, fibrinolysin, renin, subtilisin, aspergillopeptidase A, collagenase, clostridiopeptidase B, kallikrein, gastrisin, cathepsin D, bromelin, keratinase, chymotrypsin C, pepsin C, aspergillopeptidase B, urokinase, carboxypeptidase A and B, and aminopeptidase); (2) carboxylate ester



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hydrolase including carboxyl esterase, lipase, pectin esterase, and chlorophyllase; and (3) enzymes having high perhydrolysis to hydrolysis ratios. Especially effective among them are lipases, as well as esterases that exhibit high perhydrolysis to hydrolysis ratios, as well as protein engineered esterases, cutinases, and lipases, using the primary, secondary, tertiary, and/or quaternary structural features of the perhydrolases of the present invention.

**[102]** Additionally, it is contemplated that the stable compositions of the present invention may comprise additional enzymes. It is contemplated that by using combinations of enzymes, there will be a concurrent reduction in the amount of chemicals needed. The additional enzymes include but are not limited to: microbial cell wall-degrading and glycoprotein-degrading enzymes, lysozyme, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, endoglucanases, PNGases, amylases, etc., as well as mixtures thereof. In some embodiments, enzyme stabilizers may also be included in the stable composition.

**[103]** It is not intended that the present invention be limited to any specific enzyme for the generation of hydrogen peroxide, as any enzyme that generates $H_2O_2$ and acid with a suitable substrate finds use in the methods of the present invention. For example, lactate oxidases from *Lactobacillus* species which are known to create $H_2O_2$ from lactic acid and oxygen find use with the present invention. Indeed, one advantage of the methods of the present invention is that the generation of acid reduces the pH of a basic solution to the pH range in which the peracid is most effective in bleaching (*i.e.*, at or below the pKa).

**[104]** Other enzymes (*e.g.*, alcohol oxidase, ethylene glycol oxidase, glycerol oxidase, amino acid oxidase, etc.) that can generate hydrogen peroxide also find use with ester substrates in combination with the acyl transferase or other perhydrolase enzymes of the present invention to generate peracids. Enzymes that generate acid from substrates without the generation of hydrogen peroxide also find use in the present invention. Examples of such enzymes include, but are not limited to proteases. Thus, as described herein, the present invention provides definite advantages over the currently used methods and compositions for decontaminant formulation and use, as well as various other applications.

**[105]** In addition, oxidases find use in the present invention, including carbohydrate oxidases selected from the group consisting of aldose oxidase (IUPAC classification EC1.1.3.9), galactose oxidase (IUPAC classification EC1.1.3.9), cellobiose oxidase



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(IUPAC classification EC1.1.3.25), pyranose oxidase (IUPAC classification EC1.1.3.10), sorbose oxidase (IUPAC classification EC1.1.3.11) and/or hexose oxidase (IUPAC classification EC1.1.3.5), glucose oxidase (IUPAC classification EC1.1.3.4) and mixtures thereof.

**[106]** Indeed, it is contemplated that any suitable oxidase can be used in the present invention that follows the equation:

Enzyme + reduced substrate → oxidized substrate + $H_2O_2$.

***4. Hydrogen Peroxide Source***

**[107]** The present invention provides a stable composition comprising a hydrogen peroxide source. In some embodiments, the hydrogen peroxide source is a solid compound that generates hydrogen peroxide upon addition to water. Such compounds include adducts of hydrogen peroxide with various inorganic or organic compounds, of which the most widely employed is sodium carbonate perhydrate, also referred to as sodium percarbonate.

**[108]** Inorganic perhydrate salts are one preferred embodiment of hydrogen peroxide source. Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts.

**[109]** Other hydrogen peroxide adducts useful in the compositions of the present invention include adducts of hydrogen peroxide with zeolites, or urea hydrogen peroxide.

**[110]** The hydrogen peroxide source compounds may be included as the crystalline and/or substantially pure solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

**[111]** In some embodiments, the present invention provides a stable composition wherein the hydrogen peroxide source is an enzymatic hydrogen peroxide generation system. In one preferred embodiment, the enzymatic hydrogen peroxide generation system comprises an oxidase and its substrate. Suitable oxidase enzymes include, but are not limited to: glucose oxidase, sorbitol oxidase, hexose oxidase, choline oxidase, alcohol oxidase, glycerol oxidase, cholesterol oxidase, pyranose oxidase, carboxyalcohol oxidase, L-amino acid oxidase, glycine oxidase, pyruvate oxidase, glutamate oxidase, sarcosine



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oxidase, lysine oxidase, lactate oxidase, vanillyl oxidase, glycolate oxidase, galactose oxidase, uricase, oxalate oxidase, and xanthine oxidase.

**[112]** In some embodiments, the hydrogen-peroxide generating compounds and enzyme systems can be combined into the stable composition in their substantially pure form. In alternative embodiments, they may be combined with other components such as surfactants, sequestrants, builders, pH regulators, buffers, stabilizers, processing additives or any other known components of washing compositions, sanitising compositions, disinfecting compositions or bleach additives. In one embodiment, the stable composition comprises a detergent.

**[113]** Other compounds and enzymatic systems useful as hydrogen peroxide sources in the stable compositions of the present invention include but are not limited those described in U.S.S.N. 10/581,014, which is hereby incorporated by reference herein.

### *5. Ester Substrates and Peracids*

**[114]** It is not intended that the stable compositions of the present invention be limited to ingredients that generate only peracetic acid. Stable compositions may also be prepared that produce any of a wide range of peracids useful for cleaning, disinfecting, and decontaminating.

**[115]** Pernonanoic acids, as well as peracids made from long chain fatty acids (*i.e.*, C10-C18) or longer chains, may be generated from All-In-One compositions prepared according to the teachings of the present invention. In some preferred embodiments, the peracid is selected from peracetic acid, perproprionic, perbutanoic, perpentanoic, and perhexanoic acid, and pernonanoic acid.

**[116]** According to the present invention, a stable All-In-One composition for generating a specific peracid compound upon addition to water requires the use of an ester substrate that upon enzymatic conversion results in the desired peracid. Thus, in some embodiments, the ester substrate is a stable ester of an acid selected from the list consisting of: acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, nonanoic acid, formic acid, butyric acid, valeric acid, caproic acid, caprylic acid, decanoic acid, dodecanoic acid, myristic acid, palmitic acid, stearic acid, and oleic acid. In additional embodiments, triacetin, tributyrin, neodol esters, and/or ethoxylated neodol esters serve as ester substrates for peracid formation. Thus, exemplary acetic ester substrates include but are not limited to: methyl acetate, ethyl acetate, propyl acetate, triacetin (1, 3-diacetyloxypropan-2-yl acetate), and propylene glycol diacetate.



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**[117]** In a preferred embodiment, the ester substrate is a stable alcohol ester of an acid the enzymatic conversion of which results in the desired peracid. Thus, in one preferred embodiment, the ester substrate is any poly-alcohol ester compound, *e.g.*, a poly-ol diester such as PGDA. In another preferred embodiment, the ester substrate is a diol-diester compound.

**[118]** A wide range of ester substrates for perhydrolase enzymes (*e.g.*, acyl transferase) useful in the compositions of the present invention are disclosed in WO 05/056782, which is hereby incorporated by reference herein in its entirety.

**[119]** The ester substrates useful in the stable compositions of the present invention may be in either solid or liquid form. Generally, the ester substrate should be dry or substantially free of water that can activate the enzyme component of the composition. In preferred embodiments, the ester substrate includes less about 5%, less than about 1%, less than about 0.5%, less than about 0.1%, or even a lower percentage by weight of water.

**[120]** In some embodiments, the ester substrate is a stable liquid at room temperature, for example, propylene glycol diacetate (PGDA). In some embodiments, the ester substrate is a stable liquid, in which the enzyme and hydrogen peroxide source components of the stable composition do not dissolve. In preferred embodiments, the ester substrate is substantially free of water, thereby minimizing any activation of the enzyme and/or the hydrogen peroxide source in the composition prior to its use.

### *6. Adjunct Materials and Additional Components*

**[121]** Additional components find use in the formulations of the present invention. Although it is not intended that the formulations of the present invention be so limited, various components are described herein. Indeed, while such components are not essential for the purposes of the present invention, the non-limiting list of adjuncts illustrated hereinafter are suitable for use in the instant compositions and may be desirably incorporated in certain embodiments of the invention, for example to assist or enhance cleaning performance, for treatment of the substrate to be cleaned, or to modify the aesthetics of the cleaning composition as is the case with perfumes, colorants, dyes or the like. It is understood that such adjuncts are in addition to the enzymes of the present invention, hydrogen peroxide and/or hydrogen peroxide source and material comprising an ester moiety. The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of



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the cleaning operation for which it is to be used. Suitable adjunct materials include, but are not limited to, surfactants, builders, chelating agents, dye transfer inhibiting agents, deposition aids, dispersants, corrosion inhibitors, additional enzymes, and enzyme stabilizers, catalytic materials, bleach activators, bleach boosters, preformed peracids, polymeric dispersing agents, clay soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, perfumes, structure elasticizing agents, carriers, hydrotropes, processing aids and/or pigments. In addition to the disclosure below, suitable examples of such other adjuncts and levels of use are found in U.S. Patent Nos. 5,576,282, 6,306,812, and 6,326,348, herein incorporated by reference. The aforementioned adjunct ingredients may constitute the balance of the cleaning compositions of the present invention.

**[122]** In some embodiments, the enzyme system of the present invention further comprises enzymes that remove any residual peracid and/or $H_2O_2$ after decontamination has been achieved. Such enzymes include but are not limited to catalases and/or hydrolytic enzymes.

**[123]** Importantly, the present invention provides means for effective cleaning, bleaching, and disinfecting over broad pH and temperature ranges. In some embodiments, the pH range utilized in this generation is 4-12. In some alternative embodiments, the temperature range utilized is between about 5° and about 90°C. The present invention provides advantages over the presently used systems (*See e.g.*, EP Appln. 87-304933.9) in that bleaching is possible at the optimum pH of peracid oxidation, as well as providing bleaching at neutral pH, acidic pHs, and at low temperatures.

**IV. Preparation and Use of Stable Compositions for Generating Peracid Solutions**

**[124]** One key advantage of the stable compositions of the present invention is that they are "All-In-One" formulations where all the ingredients are in one container. These stable All-In-One compositions also have the advantage of easy preparation simply by combining the ingredients (*e.g.*, enzyme, hydrogen peroxide source, and ester substrate) in a suitable vessel or container. The order of mixing the ingredients is not particularly important and generally the various ingredients can be added sequentially.

**[125]** In some embodiments, all of the ingredients of the composition are solids which are simply combined by mixing. In other embodiments, at least one of the ingredients, typically the ester substrate, is a liquid, and preparation is by mixing the dry solid ingredients into the liquid.

**[126]** Preferably, the stable composition is prepared using solid forms of enzyme(s) and hydrogen peroxide generating compound(s) and mixing them so they are



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suspended in a liquid form of substrate ester compound. In one preferred embodiment, the stable composition of the present invention comprises an acyl transferase enzyme, a hydrogen peroxide source, and the liquid ester substrate, PGDA.

**[127]** In one preferred embodiment, the solid ingredients may be combined in a "dry formulation" (*e.g.*, acyl transferase enzyme + percarbonate) which is then added to a liquid ester substrate so as to create a suspension. *See e.g.*, preparation of the All-In-One composition disclosed herein in Example 9.

**[128]** In one preferred embodiment, the solid ingredients of the stable composition are used as-is. For example, granules or powder of sodium percarbonate (*i.e.*, straight out of a commercially obtained reagent jar) are combined in a container with crude solid or granules of acyl transferase, then added to the liquid PGDA to create a suspension. In alternative embodiments, the solid ingredients can be treated prior to combining with each other, or prior to addition to any liquid phase. Examples of such treatments could include encapsulation of enzyme granules and/or peroxide generating compounds in order to inhibit activity during storage, or effect slower release over time after addition to water.

**[129]** Generally, the stability of the composition is highly dependent on preventing any enzymatic conversion of the substrate, and/or generation of hydrogen peroxide, prior to use. In embodiments where all of the composition ingredients are in solid form, this is accomplished primarily by keeping the mixed ingredients dry or substantially water-free (*i.e.*, less than about 2%, 1%, or 0.5% water by weight). Even relatively small amounts of water that can allow enzyme activity and/or hydrogen peroxide generation to occur should be avoided in order to maximize stability of the All-In-One composition. Consequently, in some embodiments the stable composition further comprises a dessicant or drying agent (*e.g.*, zeolite compound, molecular sieves, etc.).

**[130]** In one embodiment, the enzyme(s) is incorporated into the stable composition in the form of granules or a spray-dried coating of enzyme-containing crude extract. In other embodiments, the enzyme(s) used in the composition is substantially purified and in a granular, spray-dried, lyophilized, or otherwise dry solid form. In some embodiments, enzyme granules are used which have been formulated so as to contain an enzyme protecting agent and a dissolution retardant material (*i.e.*, material that regulates the dissolution of granules during use).

**[131]** The present invention can be employed in connection with any number of processes for making dry enzyme granules or dry formulations of hydrogen peroxide source compounds, such as Enzoguard® (Genencor International Inc., Rochester, N.Y.) described



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in U.S. Pat. No. 5,324,649, (which is hereby incorporated by reference herein), or Savinase granules (Novo Nordisk, Denmark), among others. Other exemplary dry formulation processes for enzymes or other compounds which can be used to make the compositions of the present invention include those disclosed in, U.S. Pat. Nos. 4,106,991. 4,689,297, 5,814,501, 5,879,920, 6,248,706, 6,413,749, 6,534,466, or PCT publications WO 97/12958, WO 99/32613, WO 01/29170, and those techniques described in "Enzymes in Detergency," ed. Jan H. van Ee, et al., Chpt. 15, pgs. 310-312 (Marcel Dekker, Inc., New York, N.Y. (1997)); each of which is hereby incorporated by reference herein.

**[132]** The amounts of hydrogen peroxide source and ester substrate used in the stable composition depends on the specific compounds used as well as the enzyme and final concentration of peracid. Generally, the enzymatic generation of a peracid requires an equimolar amount of hydrogen peroxide and the corresponding ester substrate compound. Consequently, in one preferred embodiment the weight percentage of each of the hydrogen peroxide source and the substrate depends on the formula weight of the specific compounds and is selected so that there are equimolar amounts of hydrogen peroxide and substrate.

**[133]** The enzyme is incorporated into the composition as much as required according to the purpose. Generally, enzyme should preferably be incorporated in an amount of 0.00001 to 5 weight percent, and more preferably 0.02 to 3 weight percent. Where crude enzyme is used, the granules are added to the stable composition in such an amount that the purified enzyme is 0.001 to 50 weight percent in the granules. Relatively smaller amounts by weight are used with increasing enzyme purity. The granules are used in an amount of 0.002 to 20 and preferably 0.1 to 10 weight percent. Ultimately, specific amounts of enzyme will depend to some extent on the particular enzyme's empirically determined activity for a particular peracid application.

**[134]** For example, in one preferred embodiment, the stable composition comprises the acyl transferase enzyme from *M. smegmatis* (MsAcT), sodium percarbonate, and propylene glycol diacetate (PGDA), wherein the enzyme and percarbonate are solids suspended in the liquid PGDA, and whereby upon addition to water, the stable composition is capable of generating at least about 0.16% by weight peracetic acid solution. Because of the high ratio of PAA to acetic acid produced by the composition, an aqueous solution of 0.16% by weight PAA has a pH about 8.6. In some embodiments, longer mixing/reaction times for the composition in water can result in even higher levels of PAA (*e.g.*, 0.18% by weight) with lower pH (*e.g.*, about pH 8.0).



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**[135]** In this embodiment, the composition is prepared by mixing a dry formulation of enzyme and percarbonate into the liquid PGDA. The resulting stable composition is a liquid suspension preferably comprising: from about 0.001% to about 1% by weight MsAcT, from about 35% to about 45% by weight sodium percarbonate, and from about 65% to about 55% by weight propylene glycol diacetate. The stability of this liquid suspension is demonstrated by the fact that the weight percent of peracetic acid it produces in a set amount of water does not decrease significantly despite prior storage of the composition at ambient temperature for at least 7 days, about 14 days, about 30 days, about 60 days, or longer.

**[136]** The use of the stable compositions of the present invention to prepare an aqueous solution is straightforward: simply add the composition to an appropriate amount of water and stir. Generally, only purified (*e.g.*, MilliQ water), distilled, sterilized and/or deionized water is used. Thus, the present invention also provides a method for preparing a peracid solution comprising adding the stable composition to water and mixing for at least about 30 minutes, 20 minutes, 15 minutes, 10 minutes, 5 minutes, or even fewer minutes. In some embodiments, the method of preparation comprises: (a) providing a stable composition comprising an enzyme with perhydrolase activity, wherein said activity comprises a perhydrolysis to hydrolysis ratio of at least 2:1; a hydrogen peroxide source; and an ester substrate; and (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about 0.16% peracetic acid by weight, and a pH less than about 9.0. In one embodiment, the composition and the water comprise no other ingredients capable of buffering the pH.

**[137]** In preferred embodiments, the method of preparation comprises: (a) providing a stable composition comprising an acyl transferase enzyme, a hydrogen peroxide source, and propylene glycol diacetate; and (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about 0.16% peracetic acid by weight.

**[138]** It is contemplated that in addition to pure water, the stable compositions can be used in various aqueous systems, including those that have a large percentage of water (*e.g.*, more than about 85%, or more than about 95% water), as well as those with lower percentages of water (*e.g.*, less than about 85%). Alternative embodiments are contemplated where the stable composition is added to aqueous buffer solutions, and/or solutions comprising other ingredients such as surfactants, cleaning compositions, or detergent formulations. In such embodiments, the other ingredients included in the aqueous



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solution can affect the catalytic activity of the peracid generating enzyme. Adjustments to the enzyme concentration, stirring time, temperature, and/or other parameters related to the use of the stable composition are within the knowledge of, or may be determined empirically by, one of ordinary skill in the art.

**[139]** Generally, the stable compositions of the present invention are intended to be used by adding to water at typical ambient temperatures of about 18°C to about 25°C, or about 20°C to about 22°C. In some applications, however, it may be preferred to use the stable compositions at lower or higher temperatures. The stable compositions are capable of functioning over wide temperature ranges (*e.g.*, from about 5°C to about 90°C; from about 16°C to about °60C; and from about 20°C to about 37°C). Generally, the functional temperature range is dependent on the ability of the enzyme to maintain sufficient activity. Thus, in one embodiment, the present invention contemplates a stable composition comprising wild-type or engineered enzymes with high thermal stability.

**[140]** Furthermore, the present invention provides systems and kits for generating peracids in aqueous solution that based on the stable composition embodiments. Thus, in one embodiment the invention provides a system for generating peracetic acid in aqueous solution comprising any of the stable compositions of the present invention in a water soluble container. In some embodiments, the container is formed from a water soluble polymer, preferably a polyvinyl alcohol polymer. Generally, the water soluble container can be in any form, preferably a sachet, ampoule, capsule or sphere. In one preferred embodiment, the water soluble container is a sachet comprising a polyvinyl alcohol film.

### V. Water Soluble Containers

**[141]** Water soluble containers useful for delivering the stable compositions of the present invention can be in the form of a sachet, a capsule, or other blow-molded shapes, an injected molded ampoule, or other injection-molded shapes, or rotationally-molded spheres or capsules are formed from a water soluble thermoplastic resin.

**[142]** Water soluble plastics which may be useful for forming the container include low molecular weight and/or chemically modified polylactides; such polymers have been produced and sold under the name HEPLON™ (Chronopol, Inc.).

**[143]** In one embodiment, the water soluble containers useful with the present invention comprise melt processable polyvinyl alcohol resins (PVA). Such resins include VINEX™; (Texas Polymer Services, Inc.) and MONOSOL™ film (ChrisCraft Film). Any number or



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combination of PVA resins can be used. Such water soluble polymers are described in *e.g.*, U.S. Patent Nos. 6,956,070, 7,022,656, and 7,067,575, each of which is hereby incorporated by reference herein.

**[144]** Typical resin properties are:

**[145]** 1. Glass Transition Temperature (°C) = 28 to 38; preferred is 28 to 33.

**[146]** 2. Weight Average Molecular Weight (Mw) = 15,000 to 95,000; preferred is 55,000-65,000.

**[147]** 3. Number Average Molecular Weight (Mn) = 7,500 to 60,000; preferred is 27,000 to 33,000.

**[148]** In one embodiment, the poly(vinyl) alcohol resin used is MONOSOL™ 7030 or MONOSOL™ 8630.

**[149]** Blow molded capsules can be formed from the polyvinyl alcohol resin having a molecular weight of about 50,000 to about 70,000 and a glass transition temperature of about 28 to about 33°C. Pelletized resin and concentrate(s) are fed into an extruder. The extruder into which they are fed has a circular, oval, square or rectangular die and an appropriate mandrel. The molten polymer mass exits the die and assumes the shape of the die/mandrel combination. Air is blown into the interior volume of the extrudate while the extrudate contacts a pair of split molds. The molds control the final shape of the package. While in the mold, the package is filled with the appropriate volume of liquid. The mold quenches the plastic. The liquid is contained within the interior volume of the blow molded package.

**[150]** An injection molded ampoule or capsule is formed from the poly(vinyl) alcohol resin having a molecular weight of about 50,000 to about 70,000 and a glass transition temperature of about 28 to 38°C. Pelletized resin and concentrate(s) are fed to the throat of a reciprocating screw, injection molding machine. The rotation of the screw pushes the pelletized mass forward while the increasing diameter of the screw compresses the pellets and forces them to contact the machine's heated barrel. The combination of heat, conducted to the pellets by the barrel and frictional heat, generated by the contact of the pellets with the rotating screw, melts the pellets as they are pushed forward. The molten polymer mass collects in front of the screw as the screw rotates and begins to retract to the rear of the machine. At the appropriate time, the screw moves forward forcing the melt through the nozzle at the tip of the machine and into a mold or hot runner system which feeds several molds. The molds control the shape of the finished package. The package may be filled



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with liquid either while in the mold or after ejection from the mold. The filling port of the package is heat sealed after filling is completed. This process may be conducted either in-line or off-line.

**[151]** A rotationally molded sphere or capsule is formed from the poly(vinyl) alcohol resin having a molecular weight of about 50,000 to about 70,000 and a glass transition temperature of about 28 to 38°C. Pelletized resin and concentrate are pulverized to an appropriate mesh size, typically 35 mesh. A specific weight of the pulverized resin is fed to a cold mold having the desired shape and volume. The mold is sealed and heated while simultaneously rotating in three directions. The powder melts and coats the entire inside surface of the mold. While continuously rotating, the mold is cooled so that the resin solidifies into a shape which replicates the size and texture of the mold. After rejection of the finished package, the liquid is injected into the hollow package using a heated needle or probe after filling, the injection port of the package is heat sealed.

**[152]** Other suitable resins useful for water soluble containers of the present invention include polyethylene oxides (*e.g.*, POLYOX™; Union Carbide, Inc.) and cellulose derived water soluble carbohydrates (*e.g.*, METHOCEL™; Dow Chemical, Inc.). Typically, the cellulose derived water soluble polymers are not readily melt processable.

**[153]** In some embodiments, the water soluble container is a sachet. In one particularly preferred embodiment, the sachet may be formed from PVA film. Such PVA film sachets are commercially available (Solupak, Ltd., UK).

**[154]** Generally, PVA film sachets useful with the present invention may be commercially obtained (*e.g.*, from Solupak, Ltd., UK), or may be manufactured using polymer film manufacturing techniques well-known in the art. For example, the pelletized, pre-dried, melt processable PVA resin, is fed to a film extruder. The feed material may also contain pre-dried color concentrate which uses a PVA carrier resin. Other additives, similarly prepared, such as antioxidants, UV stabilizers, anti-blocking additives, etc. may also be added to the extruder. The resin and concentrate are melt blended in the extruder. The extruder die may consist of a circular die for producing blown film or a coat hanger die for producing cast film. Circular dies may have rotating die lips and/or mandrels to modify visual appearance and/or properties.

**[155]** Typical PVA film properties useful for the water-soluble sachets of the present invention include:

1. Tensile strength (125 mil, break, 50% RH) = 4,700 to 5,700 psi.



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2. Tensile modulus (125 mil, 50% RH) = 47,000 to 243,000 psi; preferred range is 140,000 to 150,000 psi.

3. Tear resistance (mean) (ASTM-D-199 gm/ml) = 900-1500.

4. Impact strength (mean) (ASTM-D-1709, gm) = 600-1,000.

5. 100% Elongation (mean) (ASTM-D-882, psi) = 300-600.

6. Oxygen transmission (1.5 mil, 0% RH, 1 atm) = 0.0350 to 0.450 cc/l00 sq. in./24 h.

7. Oxygen transmission (1.5 mil, 50% RH, 1 atm) = 1.20 to 1.50 cc/100 sq. in./24 h.

8. 100% modulus (mean) (ASTM-D-882, psi) = 1000-3000.

9. Solubility (sec) (MSTM-205,75°F.) disintegration=1-15; dissolution =10-30.

**[156]** The extruded film is slit to the appropriate width and wound on cores. Each core holds one reel of film. The reels of slit film are fed to either a vertical form, fill, seal machine (VFFS) or a horizontal form, fill, seal machine (HFFS). The Form, Fill, Seal machine (FFS) makes the appropriate sachet shape (cylinder, square, pillow, oval, etc.) from the film and seals the edges longitudinally (machine direction seal). The FFS machine also makes an end seal (transverse direction seal) and fills the appropriate volume of non-aqueous liquid above the initial transverse seal. The FFS machine then applies another end seal. The liquid is contained in the volume between the two end seals.

**[157]** In one embodiment, the PVA film used is MONOSOL™ having a weight average molecular weight range of about 55,000 to 65,000 and a number average molecular weight range of about 27,000 to 33,000.

**VI. Kits**

**[158]** The stable compositions of the invention described herein are particularly amenable to packaging in various kits. In one embodiment, the present invention provides a kit for decontamination comprising a pre-measured amount of any of the stable compositions described herein, wherein the stable composition comprises a perhydrolasae enzyme, a hydrogen peroxide source, and an ester substrate, and wherein the amount of the stable composition generates an aqueous solution of at least about 0.16% peracid by weight upon addition to a set volume of water, in suitable packaging. In some embodiments, the kit further comprises instructions for use of the stable composition in a method for decontamination as described herein. Instructions may be provided in printed form or in the form of an electronic medium such as a floppy disc, CD, or DVD, or in the form of a website address where such instructions may be obtained.



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**[159]** In one preferred embodiment, the stable composition is provided in a water soluble sealed container. In one preferred embodiment, the water soluble container of the kit is in the form of a sachet, a capsule, an ampoule, spheres formed from a water soluble thermoplastic resin, or other injection-molded shapes. In some embodiments, the water soluble sealed container is made of a water soluble polymer material selected from the group consisting of: polyvinyl alcohol, polyethylene oxides, cellulose derived water soluble carbohydrates, and polyactides. In one preferred embodiment, the water soluble container of the kit is a sachet made of a polyvinyl alcohol film.

**[160]** In one embodiment of the kit, kit further comprises a mixing container (or vessel) with a volume large enough to hold at least twice said set volume of water. In this embodiment, the mixing container may be a disposable bucket or beaker, optionally sterilized, that optionally contains a magnetic stir bar in the container along with the stable composition.

**[161]** In one embodiment, a sealed container comprising the stable composition is packaged inside the mixing container of the kit. Thus, usage of such a kit requires merely adding water to the mixing container with stirring.

**[162]** In another embodiment, the kit further comprises a set volume of water in a sealed container. In one embodiment, the water in the sealed container is sterilized. In one embodiment, the kit comprises the stable composition in a first sealed container and water in a second sealed container.

**[163]** In another embodiment, the kit includes a stirring device (*e.g.*, a spoon, or similar implement) and/or a magnetic stir bar packaged in the kit, but outside the sealed container. In other embodiments, the kit further comprises a separate package containing a composition for neutralizing the peracid solution after use.

## VII. Methods and Uses for Sanitizing, Disinfecting and/or Decontaminating

**[164]** The stable compositions of the present invention (and related systems and kits incorporating these compositions) can be used in a range of methods for decontaminating, disinfecting, and/or sanitizing items.

**[165]** In some embodiments, the method for decontamination of the present invention comprises: (a) providing a stable composition comprising an enzyme with perhydrolase activity, wherein said activity comprises a perhydrolysis to hydrolysis ratio of at least 2:1; a hydrogen peroxide source; and an ester substrate; and (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about



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0.16% peracetic acid by weight, and a pH less than about 9.0; and (c) exposing an item comprising a contaminant to said solution.

**[166]** In one preferred embodiment, the method for decontamination of the present invention comprises: (a) providing a stable composition comprising an acyl transferase enzyme, a hydrogen peroxide source, and propylene glycol diacetate; (b) adding said composition to water and mixing for at least 20 minutes, thereby generating an aqueous solution of at least about 0.16% peracetic acid by weight; and (c) exposing an item comprising a contaminant to said solution. In some embodiments of the method for preparing a solution, the stable composition provided comprises from about 0.001% to about 1% by weight MsAcT, from about 35% to about 45% by weight sodium percarbonate, and from about 65% to about 55% by weight propylene glycol diacetate.

**[167]** Depending on the specific type of contaminant to be removed, the step of exposing the item to the peracid solution may be performed over a wide range of time scales. For example, in certain sanitizing procedures exposure times as short as about 30 seconds, 1 minute, 5 minutes or 10 minutes may be sufficient. However, in other applications (*e.g.*, removal of biofilms), it may be necessary to expose the item for considerably longer periods of time, such as about 30 minutes, 1 hour, 6 hours, 12 hours, 24 hours, or even longer, in order to achieve adequate level of decontamination.

**[168]** Similarly, the temperature of the peracid solution during the exposure step may be adjusted depending on the particular type of contaminant. In a preferred embodiment, the exposure temperature is the ambient temperature at which the solution is prepared, *i.e.*, typically about 18-25°C. In other embodiments, higher temperatures may be used to facilitate the decontamination process. Generally, higher temperatures will accelerate the reactivity of the peracid solution thereby accelerating the decontamination process. Thus, in some embodiments, the exposure step may be carried out with the peracid solution at about 30°C, 37°C, 45°C, 50°C, 60°C, 75°C, 90°C or even higher.

**[169]** In one preferred embodiment of the methods, the stable composition is contained in a water soluble container and the container is added to the water. In one preferred embodiment, the water soluble container is a sachet, ampoule, capsule or sphere, formed from a water soluble polymer, preferably a polyvinyl alcohol polymer.

**[170]** In various embodiments, the methods of decontamination using the stable compositions are useful against a wide range of contaminants including toxins selected from the group consisting of botulinum toxin, anthracis toxin, ricin, scombroid toxin, ciguatoxin,



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tetrodotoxin, mycotoxins, and any combination thereof; and pathogens selected from the group consisting of bacteria, viruses, fungi, parasites, prions, and any combination thereof. For example, the methods disclosed herein may be used for decontamination of materials contaminated with materials including but not limited to toxic chemicals, mustard, VX, *B. anthracis* spores, *Y. pestis*, *F. tularensis*, fungi, and toxins (*e.g.*, botulinum, ricin, mycotoxins, etc.), as well as cells infected with infective virions (*e.g.*, flaviviruses, orthomyxoviruses, paramyxoviruses, arenaviruses, rhabdoviruses, arboviruses, enteroviruses, bunyaviruses, etc.). In some particularly preferred embodiments, the at least one pathogen is selected from *Bacillus spp., B. anthracis, Clostridium spp., C. botulinum, C. perfringens, Listeria spp., Pseudomonas spp., Staphylococcus spp., Streptococcus spp., Salmonella spp., Shigella spp., E. coli, Yersinia spp., Y. pestis, Francisella spp., F. tularensis, Camplyobacter ssp., Vibrio spp., Brucella spp., Cryptosporidium spp., Giardia spp., Cyclospora spp.*, and *Trichinella spp.*

**[171]** A biofilm is a collection of microorganisms embedded in a matrix of extracellular polymeric substances and various organic and inorganic compounds. Although some biofilms may contain a single species of microorganism, typically biofilms comprise not only different species of microorganisms but different types of microorganisms, for example algae, protozoa, bacteria and others. It has been found that one of the characterizing features of biofilms is that the microorganisms therein act cooperatively or synergistically. Empirically it has been found that microorganisms living in a biofilm are better protected from biocides than microorganisms living outside a biofilm. Thus, removal of pathogenic biofilms represents a particularly difficult problem in decontaminating and/or sanitizing equipment .

**[172]** The peracid solutions generated using the stable compositions of the present invention and the methods of their use are effective at decontaminating biofilms. In one embodiment, the stable composition made be used to generate a peracid solution useful to remove biofilms, including those formed by one or more pathogenic bacteria selected from the group consisting of: *Bacillus spp., B. anthracis, Clostridium spp., C. botulinum, C. perfringens, Listeria spp., Pseudomonas spp., Staphylococcus spp., Streptococcus spp., Salmonella spp., Shigella ssp., E. coli, Yersinia spp., Y. pestis, Francisella spp., F. tularensis, Camplyobacter ssp., Vibrio spp., Brucella spp., Cryptosporidium spp., Giardia spp., Cyclospora spp., Trichinella spp.*, and any combination thereof. In one preferred embodiment, a peracid solution made by the methods of the present invention may be used to decontaminate biofilms selected from group consisting of: *Pseudomonas aeruginosa,*



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*Staphylococcus aureus* (SRWC-10943), *Listeria monocytogenes* (ATCC 19112), and any combination thereof.

**[173]** In one preferred embodiment, pathogenic biofilms comprising bacterial cultures of *Pseudomonas spp., Staphylococcus spp.,* and/or *Listeria spp.*, contaminating stainless steel equipment can be substantially removed (*i.e.*, ~ 500-1000-fold reduction) by exposure to a 0.16% by weight PAA solution (generated from the stable composition) at 45°C for 45 minutes.

**[174]**

**[175]** In various embodiments, the methods of decontamination using the stable compositions are useful for decontaminating a wide range of contaminated items including hard surfaces, fabrics, food, feed, apparel, rugs, carpets, textiles, medical instruments, veterinary instruments, sanitize, and stainless steel items and equipment, including large reactors, used in pharmaceutical and biotechnology processes.

**[176]** The peracid solutions generated enzymatically using the stable compositions of the present invention are particularly well-suited for cleaning stainless steel items and equipment because the ratio of peracid to corresponding acid generated in aqueous solution is much higher than found in commercial solutions. For example, a PAA solution generated using the stable composition of S54V-MsAcT, percarbonate, and PGDA, will have a ratio of PAA to acetic acid of approximately 10:1. Commercial PAA solutions typically have more acetic acid than PAA and may even have the reversed ratio (1:10). The increased ratio of PAA to acetic acid reduces, or completely obviates, the need to carry out further passivating treatments of the stainless steel item or equipment following the PAA treatment. Thus, in some embodiments, peracid solutions generated using the stable compositions of the present invention may be used to sanitize stainless steel items and equipment, including large reactors, used in pharmaceutical and biotechnology processes. In preferred embodiments, the peracid solutions may be used to sanitize stainless steel items and equipment in a single-step, without the need for any further treatment of the steel with a passivating agent.

**[177]** In still further embodiments, the present invention finds use in decontamination of food and/or feed, including but not limited to vegetables, fruits, and other food and/or feed items. Indeed, it is contemplated that the present invention will find use in the surface cleaning of fruits, vegetables, eggs, meats, etc. Indeed, it is intended that the present invention will find use in the food and/or feed industries to remove contaminants from



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various food and/or feed items. In some particularly preferred embodiments, methods for food and/or feed decontamination set forth by the Food and Drug Administration and/or other food safety entities, as known to those of skill in the art find use with the present invention.

**[178]** In still further preferred embodiments, the item in need of decontamination is selected from hard surfaces, fabrics, food, feed, apparel, rugs, carpets, textiles, medical instruments, and veterinary instruments. In some particularly preferred embodiments, the food is selected from fruits, vegetables, fish, seafood, and meat. In some still further preferred embodiments, the hard surfaces are selected from household surfaces and industrial surfaces. In some particularly preferred embodiments, the household surfaces are selected from kitchen countertops, sinks, cupboards, cutting boards, tables, shelving, food preparation storage areas, bathroom fixtures, floors, ceilings, walls, and bedroom areas. In some alternative embodiments, the industrial surfaces are selected from food processing areas, feed processing areas, tables, shelving, floors, ceilings, walls, sinks, cutting boards, airplanes, automobiles, trains, and boats.

## EXAMPLES

**[179]** The following examples are provided in order to demonstrate and further illustrate certain preferred embodiments and aspects of the present invention and are not to be construed as limiting the scope thereof.

**[180]** In the experimental disclosure which follows, the following abbreviations apply: °C (degrees Centigrade); RT (room temperature); rpm (revolutions per minute); $H_2O$ (water); $dH_2O$ (distilled water); HCl (hydrochloric acid); aa (amino acid); bp (base pair); kb (kilobase pair); kD (kilodaltons); gm (grams); µg and ug (micrograms); mg (milligrams); ng (nanograms); µl and ul (microliters); ml (milliliters); mm (millimeters); nm (nanometers); µm and um (micrometer); M (molar); mM (millimolar); µM and uM (micromolar); U (units); V (volts); MW (molecular weight); sec (seconds); min(s) (minute/minutes); hr(s) (hour/hours); $MgCl_2$ (magnesium chloride); NaCl (sodium chloride); $OD_{420}$ (optical density at 420 nm); PAGE (polyacrylamide gel electrophoresis); EtOH (ethanol); LB (Luria broth); LA (Luria agar); PBS (phosphate buffered saline [150 mM NaCl, 10 mM sodium phosphate buffer, pH 7.2]); SDS (sodium dodecyl sulfate); Tris (tris(hydroxymethyl)aminomethane); w/v (weight to volume); v/v (volume to volume); wt % (weight percent); PGDA (1,2-propylene glycol diacetate); PAA (peracetic acid); Per (perhydrolase); *per* (perhydrolase gene); Ms (*M. smegmatis*); MsAcT (*M. smegmatis* acyl transferase); S54V-MsAcT or S54V



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variant (*M. smegmatis* acyl transferase variant comprising the S54V substitution); MS (mass spectroscopy); Dial (Dial Brands, Inc., Scottsdale, AZ); Kemira (Kemira Industrial Chemicals, Helsingborg, Sweden); EM Science (EM Science, Gibbston, NJ); HP (Hewlett-Packard, Palo Alto, CA); ICN (ICN Pharmaceuticals, Inc., Costa Mesa, CA); Dial (Dial, Corp., Scottsdale, AZ); Pierce (Pierce Biotechnology, Rockford, IL); Amicon (Amicon, Inc., Beverly, MA); ATCC (American Type Culture Collection, Manassas, VA); Amersham (Amersham Biosciences, Inc., Piscataway, NJ); Becton Dickinson (Becton Dickinson Labware, Lincoln Park, NJ); BioRad (BioRad, Richmond, CA); Difco (Difco Laboratories, Detroit, MI); GIBCO BRL or Gibco BRL (Life Technologies, Inc., Gaithersburg, MD); MIDI (MIDI Labs, Newark, DE); Sigma or Aldrich (Sigma-Aldrich Inc., St. Louis, MO); Sorvall (Sorvall Instruments, a subsidiary of DuPont Co., Biotechnology Systems, Wilmington, DE); Agilent (Agilent Technologies, Palo Alto, CA); Minolta (Konica Minolta, Ramsey, NJ); and Zeiss (Carl Zeiss, Inc., Thornwood, NY).

## EXAMPLE 1

### Killing Curve for *B. subtilis* Spores by Peracetic Acid (PAA)

**[181]** In this Example, experiments conducted to determine the killing curve of peracetic acid (PAA) and PAA in conjunction with detergent (commercially available PUREX® [Dial] was used in this Example) for *B. subtilis* spores. In these experiments, the *B. subtilis* spores were prepared as known in the art (*See e.g.*, Siccardi *et al.*, J. Bacteriol., 121:13-19 [1975]). Assays were carried out in duplicate in 96-well, round bottomed microtiter plates (Costar) with peracetic acid (32 wt % in acetic acid; Aldrich). The PAA was serially diluted in either 50 mM $KPO_4$ buffer, pH 7.1 ("Buffer"), or in a 1:500 dilution of Purex (original formula; Dial) in the same buffer ("Buffer + Det") in a total volume of 50 µl. The amount of PAA added to the assay was 0, 0.4, 4 or 40 mM. A volume of 5 µl of the spore suspension, containing $10^9$ -$10^{10}$ spores, was then added to each well and the assay incubated for 15 min at RT. Ice cold LB (150 µl) (*See e.g.,* Sambrook *et al.*, "Molecular Cloning: A Laboratory Manual", Second Edition (Cold Spring Harbor), [1989]) was then added to each well, mixed, and 100 µl transferred to a fresh 96-well plate. Serial dilutions of each solution were made (in a total volume of 100 µl/well). A volume of 5 µl of each dilution was spotted onto LA plates (Sambrook *et al.*, *supra*), and incubated at 37°C for 17-24 h. Colonies were counted and the % spore killing was determined relative to the respective controls (buffer alone or buffer + detergent, without peracid). The results are presented in Table 1, as an average of duplicates from one experiment. However, the experiment was done twice in



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duplicate with similar results. Based on these results, PAA in the range of about 4 to about 40 mM was determined to be sufficient to kill *B. subtilis* spores in 15 min.

**Table 1: Killing of *B. subtilis* Spores by PAA**

| | Buffer | | Buffer + Detergent | |
|---|---|---|---|---|
| [PAA] (mM) | Spores/ml | %Spore Killing | Spores/ml | % Spore Killing |
| 0 | $1.8x10^9$ | 0 | $1.6 x10^9$ | 0 |
| 0.4 | $2.4x10^8$ | 86.4 | $1.7 x10^9$ | 0.05 |
| 4 | $1.6x10^8$ | 90 | $2.4 x10^8$ | 86.4 |
| 40 | 0 | 100 | 0 | 100 |

## EXAMPLE 2
## Enzymatic Generation of PAA

**[182]** In this Example, three methods for generation of PAA by acyl transferase are described. In one method, at least one acyl transferase (wild-type or variant) is combined with at least one ester substrate, and hydrogen peroxide in a buffer or detergent, with or without one or more surfactants. In an alternative method, at least one acyl transferase (wild-type or variant), at least one ester substrate, and sodium percarbonate (or other source of $H_2O_2$) are combined in a buffer or detergent, with or without one or more other surfactants. In yet a further method, at least one acyl transferase (wild-type or variant) is combined with glucose oxidase and glucose, in a concentration sufficient to generate an amount of PAA with which to kill spores in buffer or detergent. In some formulations, one or more other surfactants are also included. Other enzymes that generate $H_2O_2$ also find use in this system, including oxidases, oxidoreductases (*e.g.*, glyerol oxidase or hexose oxidase). In some preferred embodiments, a co-factor independent alcohol oxidase is used.

***Determination of PAA Concentration***

**[183]** In these experiments, methods known in the art were used to determine the concentration of PAA (*See e.g.*, Pinkernell *et al.*, Analyst, 122:567-571 [1997]). In this ABTS assay, 100 µl of the solution to be analyzed was added to 1 ml of 125 mM potassium citrate buffer, pH 5.0, containing 1.0 mM 3-ethylbenzthiazoline-6-sulfonic acid (ABTS) and 50 uM KI, and allowed to incubate at RT for 3 minutes. The absorbance was measured at 420 nm in a HP 8452A Diode Array Spectrophotomer and compared to a standard curve prepared using authentic standard. The enzymatic reactions to form PAA were initiated with addition of enzyme and conducted at RT. Aliquots were withdrawn from the reactions at the indicated times and analyzed for PAA concentration. The sodium percarbonate used in



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these experiments was obtained from Kemira and the hydrogen peroxide was obtained from EM Science.

***Comparison of PAA Enzymatically Generated from $H_2O_2$ or Sodium Percarbonate***

**[184]** A solution of 39 mM sodium percarbonate (sodium carbonate peroxyhydrate, Technical grade 85%, yielding 100 mM effective $H_2O_2$; Kemira) was prepared in 320 mM $KPO_4$ pH 7.1. After dissolution of the solid percarbonate, the resulting solution had a pH of 7.6. To compare the enzymatic production of PAA from prepared $H_2O_2$ (32 wt %, Aldrich) or $H_2O_2$ formed from percarbonate under identical pH conditions, two reactions were prepared. One reaction contained 100 mM $H_2O_2$ in 320 mM $KPO_4$, pH 7.6, 100 mM 1,2-propylene glycol diacetate (Aldrich), and 2 ppm variant S54V. The absolute concentration of $H_2O_2$ was assumed from the value stated on the label and not confirmed by analysis. The second reaction contained 39 mM sodium percarbonate in 320 mM $KPO_4$, pH 7.1, 100 mM 1,2-propylene glycol diacetate, and 2 ppm S54V. The reactions were initiated by the addition of the enzyme. Samples were withdrawn at the times indicated and the concentration of PAA determined as described in Example 1.

**[185]** The results for PGDA as substrate are shown in Figure 1. As indicated in Figure 1, the progress of the reaction and final concentration of PAA is similar in both cases.

**[186]** In order to study the use of different propyl alcohol acetate ester substrates, the generation of PAA was carried out using the same general method described above for PGDA, but using either propyl acetate or triacetin as the ester substrate. It was observed that these other two ester substrates also reacted in the system with S54V-MsAcT to make PAA. The relative conversion rate to PAA for the three ester substrates was observed to be: PGDA > triacetin > propyl acetate.

## *EXAMPLE 3*

## Enzymatic Generation of PAA Kills *B. subtilis* Spores

**[187]** In this Example, experiments conducted to assess the killing ability of enzymatically generated PAA tested with *B. subtilis* spores are described. Based on the results obtained in the experiments described in Examples 1 and 2, a range of 4 to 40 mM PAA was determined to be sufficient to demonstrate killing of spores of *B. subtilis* I-168. In these experiments, spore killing was assessed in buffer, as well as in detergent.

***Spore Killing in Buffer***

**[188]** In this experiment, sodium percarbonate was used as the source of $H_2O_2$. The final solution contained: 100 mM 1,2-propylene glycol diacetate, 2 ppm S54V variant, 39 mM



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sodium percarbonate (Technical grade 85%; yielding 100 mM effective $H_2O_2$) in 320 mM $KPO_4$ pH 7.1 in a total volume of 800 µl. This mix (yield 40 mM PAA) was serially diluted to give additional mixes that yielded 4.9, 9.9 and 20.5 mM PAA. A mix with only 400 mM $KPO_4$ pH 7.1 was used to determine total spore counts in the absence of PAA. The mixes were allowed to incubate at room temperature for 3 min. A volume of 180 µl of each of the mixes was then dispensed into duplicate wells of a round-bottomed 96-well plate (Costar) that contained 20 µl of the spore suspension used in Example 1, to yield a total volume of 200 µl in each well. The liquid was gently pipetted 4-5 times to ensure mixing of the components. The mixes were incubated with the spores for a further 15 or 30 minutes at room temperature. At the 15 and 30 minute time points, 20 µl were removed from each of the wells, added to wells in a fresh 96-well plate and serially diluted in LB to $10^{-7}$ in a total volume of 100 µl. A volume of 5 µl from each dilution of each spore mixture was spotted onto an LA plate, allowed to dry and then incubated overnight at 37°C. Also at the 15 and 30 min time points, an appropriate volume was removed from each well and diluted sufficiently in $dH_2O$ to yield a measurable amount of PAA using the ABTS assay on scale with a standard, as described in Example 1. Results of these assays are shown in Table 2. The results of the spore killing are presented as an average of the duplicates.

**Table 2: Use of MsAcT System to Generate PAA to Kill *B. subtilis* Spores in Buffer**

| [PAA] (mM) (Theoretical) | [PAA] Generated (mM) (15 min) | Spores/ml 15 min | %Spore Killing 15 min | [PAA] Generated (mM) (30 min) | Spores/ml 30 min | %Spore Killing 30 min |
|---|---|---|---|---|---|---|
| 0 | 0 | $1.5x10^9$ | 0 | 0 | $1.5 x10^9$ | 0 |
| 4.9 | 2.2 | $9 x10^8$ | 40 | 2.4 | $9.4 x10^8$ | 37 |
| 9.9 | 6.1 | $1 x10^8$ | 93.3 | 7.1 | $5 x10^7$ | 96.7 |
| 20.5 | 15 | $4.4 x10^4$ | 99.997 | 18 | 0 | 100 |
| 39.5 | 35 | 0 | 100 | 41 | 0 | 100 |

***Spore Killing in Detergent.***

**[189]** The experiment was repeated exactly as described except that a 1:500 dilution of Purex in 320 mM $KPO_4$ pH 7.1, was used in place of the buffer. The results are presented in Table 3 (average of duplicates). Controls included various reaction components in 400 mM $KPO_4$ pH 7.1 buffer: 2 ppm S54V variant, 2 ppm S54V variant with 39 mM percarbonate, 100 mM 1,2-propylene glycol diacetate, 100 mM 1,2-propylene glycol diacetate with 39 mM sodium percarbonate, 39 mM sodium percarbonate. All these treatments gave equivalent levels of spores/ml after a 30 min incubation, except sodium percarbonate alone ($1x10^9$ spores/ml vs $5x10^9$ spores/ml for other controls). This decrease was not seen with



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sodium percarbonate in combination with other components and was certainly not as dramatic as the killing seen by the mixture of all 3 components at comparable levels (100% killing).

**Table 3: Use of MsAcT System to Generate PAA to Kill *B. subtilis* Spores in Detergent**

| [PAA] (mM) (Theoretical) | [PAA] Generated (mM) (15 min) | Spores/ml 15 min | %Spore Killing 15 min | [PAA] Generated (mM) (30 min) | Spores/ml 30 min | %Spore Killing 30 min |
|---|---|---|---|---|---|---|
| 0 | 0 | $2x10^9$ | 0 | 0 | $2x10^9$ | 0 |
| 4.9 | 3.7 | $2x10^9$ | 0 | 3.3 | $5x10^8$ | 75 |
| 9.9 | 8.9 | $1.7x10^9$ | 91.5 | 8.1 | $4x10^7$ | 98 |
| 20.5 | 19.6 | $3x10^5$ | 99.99 | 18.9 | 0 | 100 |
| 39.5 | 44.5 | 0 | 100 | 40.4 | 0 | 100 |

## EXAMPLE 4

### Enzymatic Generation of PAA to Kill *Trichoderma reesei* Spores

**[190]** In this Example, experiments conducted to assess the killing ability of PAA on T. *reesei* spores are described. *T. reesei* spores were prepared by growing the strain for approximately 4 days on Potato Dextrose (PDA) media at 30°C. When the plate was approximately 75% covered by fungal growth, it was incubated at room temperature for several days until there was confluent growth. The spores were scraped off the plate using a cotton-tipped swab, resuspended in 1 ml of 10% glycerol and frozen at –80°C until used. Prior to use in the spore killing assay, the spore suspension was thawed, the spores pelleted by centrifugation, washed twice with 1 ml $dH_2O$, and resuspended in 1 ml of $dH_2O$. The spore killing experiments were carried out as described in Example 3, except that 20 µl of the fungal spore preparation were added to the wells of the 96-well plate instead of the *Bacillus* spores. Also, the mixes were made up such that the amount of PAA generated was 40, 13.3, 4.4 and 1.5 mM. The dilutions of the 15 and 30 minute incubations were plated on PDA media. The actual amount of PAA generated was determined as described in Example 1, at the 15 and 30 minute time points. The results are presented in Table 4. These results indicate that fungal spores were killed by PAA generated by the MsAcT system and at a lower level of PAA than the *B. subtilis* spores.



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**Table 4. Use of MsAcT System to Generate PAA to Kill *Trichoderma reesei* Spores**

| [PAA] Generated (mM) (Theoretical) | [PAA] Generated (mM) 15 min | Spores/ml 15 min | %Spore Killing 15 min | [PAA] Generated (mM) 30 min | Spores/ml 30 min | %Spore Killing 30 min |
|---|---|---|---|---|---|---|
| 0 | 0 | $2x10^{10}$ | 0 | 0 | $2x10^{7}$ | 0 |
| 1.5 | 0.41 | $2x10^{3}$ | 99.99 | 0.3 | $2x10^{3}$ | 99.99 |
| 4.4 | 2.1 | 0 | 100 | 2.2 | 0 | 100 |
| 13.3 | 10 | 0 | 100 | 8.5 | 0 | 100 |
| 40 | 42 | 0 | 100 | 38 | 0 | 100 |

## EXAMPLE 5
## PAA Production from Glucose and PGDA

**[191]** In this Example, experiments to assess the amount of peracetic acid produced from glucose and propyleneglycol diacetate are described. A 15 ml solution was prepared containing 50 mM $KPO_4$ pH 7.1 with 60 mM glucose, and 20 mM 1,2-propylene glycol diacetate (Aldrich). The solution was continuously sparged with air and stirred at room temperature. The reaction to generate $H_2O_2$ was initiated by the addition of 100 Units of glucose oxidase (Oxygen HP, Genencor International) and allowed to proceed for 1 hr. A sample was withdrawn and tested for PAA before the addition of 2 ppm S54V variant, to initiate the production of PAA from the formed $H_2O_2$. The results are presented in Figure 2. Further samples were withdrawn at the times indicated in Figure 2, and the concentration of PAA determined as described above. No PAA was detected before the addition of enzyme and approximately 9.5 mM PAA was produced from the 20 mM 1,2-propylene glycol diacetate and the $H_2O_2$ produced from the glucose/ glucose oxidase reaction.

## EXAMPLE 6
## Generation of PAA by MsAcT at Different Temperatures

**[192]** In this Example, experiments were conducted to assess the generation of peracetic acid by MsAcT at different temperatures are described. Such generation provides means to resolve problems associated with storage instability of PAA at various temperatures. In these experiments, MsAcT is used to generate PAA over a range of temperatures from about 20°C to about 60°C. In some experiments, temperatures such as 21°C, 40°C, and 60°C are used.

**[193]** In these experiments, three reactions were prepared, consisting of 320 mM $KPO_4$ pH 7.1, 100 mM 1,2-propylene glycol diacetate (Aldrich), and 100 mM sodium percarbonate. The reactions were equilibrated at 21°C, 40°C and 60°C, and then initiated by the addition



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of S54V variant to a final concentration of 2 ppm. The results are presented in Figure 3. Samples were withdrawn at the times indicated in the Figure, and the concentration of PAA determined as described above. These results indicate that the enzyme system is functional at least up to 60°C.

## EXAMPLE 7
### Generation of Concentrated Peracetic Acid by MsAcT

**[194]** In this Example experiments were conducted to determine the ability of MsAcT to generate a concentrated solution of peracetic acid. These experiments were conducted in order to address the potential benefit of preparing a concentrated peracetic acid solution which is suitable for dosing or dilution into different solutions for use. In this experiment the reaction contained 50 mM $KPO_4$, 2 M $H_2O_2$ (EM Science), 2 M 1,2-propylene glycol diacetate (Aldrich), and the S54V variant to a final concentration of 160 ppm. The reaction was vortexed occasionally to mix the reactants, as they were not miscible at this concentration. Mixing was conducted at room temperature. The results are shown in Figure 4. Samples were diluted at the indicated times and the peracetic acid concentration was determined as described above.

## EXAMPLE 8
### An Enzymatic PAA Generating System With High Sporicidal Activity

**[195]** This example illustrates the effectiveness of a 0.16% by weight peracetic acid (PAA) solution, generated using a three component formulation of the S54V mutant of the acyl transferase enzyme from *M. smegmatis* (S54V-MsAcT), 1,2-propylene glycol diacetate (PGDA) (as ester substrate), and sodium percarbonate (as hydrogen peroxide source), in a number of EPA approved decontamination assays.

***Materials and Methods***

**[196]** Preparation of 250 mL PAA test solution: A dry formulation was made up in 15 mL conical tubes, each containing from about 1.20 g to about 1.30 g sodium percarbonate, and from about 26.0 mg to about 31.9 mg of granules of S54V-MsAcT enzyme. For each dry formulation tube, a separate 15 mL conical tube was prepared containing 1.8 mL of the ester substrate, propylene glycol diacetate (PGDA). One dry formulation tube was packaged with one PGDA tube in a single zip lock bag. The contents of one zip lock bag (*i.e.*, one dry formulation tube and one PGDA tube) constituted one unit for generation of 0.16% PAA upon addition to 250 mL of water.



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**[197]** PAA test solution was prepared by adding the dry formulation from one unit into 250 mL of room temperature sterilized deionized water until fully dissolved. Some of the 250 mL test solution was used to rinse any residual dry formulation from the tube into the solution. Then the tube of PGDA liquid from was added to the stirring 250 mL solution and once again, some of the solution was used to rinse any residual PGDA from the tube into the solution. The PAA test solution was then allowed to stir for 20 minutes. The PAA test solution was homogeneous by visual inspection. It was used within two hours of preparation.

**[198]** Preparation of 2000 mL PAA test solution: A dry formulation was made up in 15 mL conical tubes, each containing from about 9.6 g to about 9.8 g sodium percarbonate, and from about 216 mg to about 226 mg of granules of S54V-MsAcT enzyme. For each dry formulation sample, a separate 15 mL conical tube was prepared containing 1.8 mL of the ester substrate, propylene glycol diacetate (PGDA). One dry formulation tube was packaged with one PGDA tube in a single zip lock bag. The contents of one zip lock bag it (*i.e.*, one dry formulation tube and one PGDA tube) constituted one unit for generation of 0.16% PAA upon addition to 2000 mL of water.

**[199]** Preparation of the 2000 mL PAA test solution was the same as described above for the 250 mL test solution except for the larger amounts of dry formulation, PGDA liquid and water.

**[200]** Assay 1: Germicidal and Detergent Sanitizing Action

**[201]** PAA test solutions were prepared according to the 250 mL recipe above. A suspension of either *Staphylococcus aureus* (ATCC 6538) or *Escherichia coli* (ATCC 11229) cells was exposed to the PAA test solution for either 30 seconds or 60 seconds. Following exposure, an aliquot was transferred to the neutralizing subculture medium (Letheen broth + 0.1% sodium thiosulfate + 0.01% catalase) and assayed for survivors utilizing pour plating techniques and Tryptone glucose extract agar (TGEA). Appropriate numbers control, purity, sterility, viability, and neutralization controls also were performed.

**[202]** Assay 2: Inanimate Non-Food Contact Surface Sanitizing Efficacy

**[203]** PAA test solutions were prepared according to the 250 mL recipe above. A film of bacterial cells dried on a surface of a glass slide carriers. Four different lots of eight slides were prepared using two different bacteria: *Staphylococcus aureus* (ATCC 6538) and *Enterobacter aerogenes* (ATCC 13048). Five of the contaminated slides were exposed to the PAA test solution for either two minutes or five minutes at 18.0°C. After exposure, the



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neutralizing subculture medium (Letheen broth + 0.1% sodium thiosulfate + 0.01% catalase) was added to each jar containing the glass slide carrier and the PAA test solution, and the solution was assayed for survivors. Three control slides from each lot were not exposed to a water solution and similarly treated with neutralizing subculture medium.

**[204]** Assay 3: AOAC Germicidal Efficacy - Use-Dilution Method

**[205]** PAA test solutions were prepared according to the 2000 mL recipe above. A film of bacterial cells was dried on the surface of a lot of 30 stainless steel carrier items. Three different lots were prepared using three different bacteria: *Pseudomonas aeruginosa* (ATCC 15442), *Staphylococcus aureus* (ATCC 6538), and *Salmonella choleraesuis* (ATCC 10708). Each of the contaminated items was exposed to the PAA test solution for either 5 minutes or 10 minutes at room temperature (20.0°C). After exposure, the items were transferred to vessels containing neutralizing subculture medium (Letheen broth + 0.1% sodium thiosulfate + 0.01% catalase) and assayed for surviving bacteria. Appropriate purity, viability, carrier item sterility, neutralizing subculture medium sterility, viability, neutralization confirmation and carrier population controls also were performed.

**[206]** Assay 4: AOAC Sporicidal Efficacy:

**[207]** PAA test solutions were prepared according to the 250 mL recipe above. A suspension of *Bacillus subtilis* (ATCC 19659) spores was dried on a lot of 30 Dacron sutures. A suspension of *Clostridium sporogenes* (ATCC 3584) was dried on a lot of 30 porcelain penicylinders. Each of the contaminated items was exposed to the PAA test solution for either 2 hours or 5.5 hours at room temperature (20.0°C). After exposure, the items were transferred to vessels containing neutralizing subculture medium (thiolglycollate medium + 0.1% sodium thiosulfate + 0.01% catalase) and assayed for surviving bacteria. Appropriate HCl, viability, purity, sterility, contaminated item quantitation, and neutralization controls also were performed.

***Results***

**[208]** Assay 1: The PAA test solution demonstrated > 99.999% reduction of either *Staphylococcus aureus* (ATCC 6538) or *Escherichia coli* (ATCC 11229) after only a 30 second exposure at 20.0°C.

**[209]** Assay 2: The PAA test solution demonstrated > 99.9% reduction of either *Staphylococcus aureus* (ATCC 6538) or *Enterobacter aerogenes* (ATCC 13048) on glass slides following two-minute (or five minute) exposure at 18.0°C.



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**[210]** Assay 3: Five minute exposure of the contaminated stainless steel carrier items to the PAA test solution resulted in no demonstrated growth in any of 30 subculture tubes of any of *Pseudomonas aeruginosa* (ATCC 15442), *Staphylococcus aureus* (ATCC 6538), and *Salmonella choleraesuis* (ATCC 10708). One of 30 items exposed for ten minutes to the PAA solution did exhibit growth of *Pseudomonas aeruginosa* (ATCC 15442), however there was no demonstrated growth for any of the other bacteria in any of the ten minute exposure subculture tubes.

**[211]** Assay 4: No demonstrated growth of *Bacillus subtilis* (ATCC 19659) in any of the 30 primary subcultures and no growth in any of the 30 secondary subcultures when tested using contaminated Dacron sutures exposed to the PAA solution for 2 hours or 5.5 hours at 20.0°C. Similarly, no demonstrated growth of *Clostridium sporogenes* (ATCC 3584) in any of the 30 primary subcultures and no growth in any of the 30 secondary subcultures when tested using contaminated porcelain penicylinders exposed to the PAA solution for 2 hours or 5.5 hours at 20.0°C.

***Conclusions***

**[212]** The 0.16% PAA solution generated using a three component formulation of S54V-MsAcT enzyme, propylene glycol diacetate (as ester substrate), and sodium percarbonate (as peroxide source), was highly effective in all four EPA approved disinfection/decontamination assays tested. The Germicidal and Detergent Sanitizing Action of Disinfectants test results show greater that 99.999% effectiveness against *Staphylococcus aureus* and *Escherichia coli*. The Standard Test Method for Efficacy of Sanitizers Recommended for Inanimate Non-Food Contact Surfaces test results show greater than 99.9% effectiveness against *Stapylococcus aureus* and *Enterobacter aerogenes*. The AOAC Use-Dilution Method test results showed 100% effectiveness against *Staphylococcus aureus*, *Salmonella choleraesius*, and 96.7% effectiveness against *Pseudomonas aeruginosa*. The Sporicidal Activity of Disinfectants (AOAC) assay demonstrated 100% efficacy of the PAA solution against *Bacillus subtilis* and *Clostridium sporogenes* spores.

## EXAMPLE 9

### A Stable "All-In-One" PAA Generating Composition With High Sporicidal Activity

**[213]** This example illustrates the preparation, and stability over time, of an "All-In-One" composition of S54V-MsAcT enzyme and sodium percarbonate in the liquid ester substrate,



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propylene glycol diacetate. The example also illustrates the use of this composition to generate a 0.16 % by weight PAA solution.

***Materials and Methods***

**[214]** All-in-One Composition: To a tube of the dry formulation (containing 1.22 g of sodium percarbonate and 28.0 mg of S54V-MsAcT granules) prepared as described in Example 8 was added 1.8 mL of PGDA liquid.

**[215]** Activation and Assay of All-in-One Composition: The All-in-One composition as prepared above was added to 250 mL of deionized water with stirring. Two additional PAA solutions were prepared according to the 250 mL and 2000 mL recipes described above in Example 8.

**[216]** At t = 20 minutes, the pH of each of these three solutions was measured and found to be 10.3. Also at t = 20 minutes, a 20 μL aliquot was taken from each of the three solutions and added to 980 μL of 125 mM sodium citrate, pH 5.0. These three diluted samples were then assayed for PAA concentration using the ABTS assay described above.

**[217]** Stability Study: Two additional All-in-One composition samples were prepared. One was maintained for 4 days before being activated in 250 mL water and assaying for PAA concentration. The other was maintained for 33 days at room temperature before being activated in 250 mL water and assaying for PAA concentration. For comparison, samples were prepared as in Example 8 with the dry formulation components maintained separately from the liquid PGDA component for the same 4 day and 33 day periods at room temperature before being activated in water.

**[218]** Variable PAA Generating Compositions: A set of five All-in-One compositions with variable amounts of sodium percarbonate were prepared to demonstrate the ability to vary the concentration of PAA generated over a range between about 60% and 160% of the standard composition. The five All-in-One composition samples were made up according to amounts listed in Table 5.

**TABLE 5**

| Sample # | Sodium percarbonate (g) | Enzyme (mg) | PGDA (mL) |
|---|---|---|---|
| 1 | 0.768 | 30.7 | 1.8 |
| 2 | 1.003 | 30.9 | 1.8 |
| 3 | 1.251 | 29.6 | 1.8 |
| 4 | 1.501 | 28.7 | 1.8 |
| 5 | 2.009 | 30.5 | 1.8 |



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**[219]** These five samples were then added to 250 mL deionized water with stirring at ambient temperature (20°C). Sample aliquots for assay were taken at 10, 20, and 30 minutes. PAA concentration was assayed using the ABTS assay in a microtiter plate.

**[220]** Sporicidal Efficacy Assay: An All-In-One composition was prepared containing 1.37 g sodium percarbonate, 33.30 mg S54V-MsAcT, mixed with 1.80 mL PGDA in a 15.0 mL conical tube. The composition was added to sterile deionized water with stirring for 20 minutes. 10 mL of the resulting PAA test solution was placed into each of four 25 x 150 mm tubes. These tubes were placed in a 20°C incubator and allowed to come to temperature. Using sterile forceps, five penicylinders, contaminated with *B. subtilis*, or five suture loops, contaminated with *B. subtilis,* were added to each tube. After the addition of all of the cylinders or sutures to each solution, a period of five minutes was allowed to make time for later removal from the tubes. After a contact time of one hour at 20°C, the penicylinders or sutures were removed, each to a separate tube of 10 mL fluid thioglycollate medium (Difco Cat. # 225650) using bent sterile plastic needles (tips bent aseptically while inside the bag into a hook). After completing transfer to the primary tube of thiolglycollate medium, the cylinders and sutures were transferred to a fresh tube of thioglycollate medium (10 mL) and incubated for 21 days at 37°C. If no growth was observed after 21 days, the tubes were heat-shocked at 80°C and re-incubated for an additional 72 hours at 37 °C. Nineteen to twenty replicates were run.

***Results***

**[221]** The All-in-One composition when activated in 250 mL of water with stirring for 20 minutes generated a solution with 0.18% peracid. The 250 mL and 2000 mL recipes prepared in the same assay yielded solutions with 0.17% and 0.17% peracid, respectively.

**[222]** The solutions prepared with the All-in-One composition maintained for 4 days and 33 days at room temperature generated 100% of the expected concentration of peracid. Similarly, the solutions prepared using the separate dry formulation and liquid components yielded essentially 100% of their expected PAA concentration.

**[223]** The five All-in-One composition samples prepared with varying amounts sodium percarbonate yielded a range of PAA concentrations from 0.11% to 0.33% at the 20 minute time point that constitutes the standard usage conditions. Thus, the All-in-One composition can be "tuned" to provide a desired PAA concentration within a specified range. In this particular example, the concentration of PAA generated ranged from 19-51 mM, which was



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28.5 – 76.5 mM $H_2O_2$ ($Na_2CO_3 \cdot 1.5H_2O_2$). The maximum conversion rate of $H_2O_2$ was 61.7% observed for sample 5 at t = 30 minutes. Based on this, a desired amount of PAA can be achieved by adjusting the percarbonate level or the PGDA level, or both.

**[224]** The All-in-One composition made with 1.37 g sodium percarbonate, 33.30 mg S54V-MsAcT, mixed with 1.80 mL PGDA in 250 mL water exhibited no failures in sporicidal efficacy for the *B. subtilis* contaminated sutures and penicylinders.

***Conclusions***

**[225]** An "All-in-One" composition containing all three components for enzymatic PAA generation in a single tube can be used to generate an effective PAA decontamination solution (0.16%) equally as well as formulations where the dry components are stored separate from the liquid PGDA ester substrate. Remarkably, the All-in-One composition exhibited stability with 0% loss of performance in PAA generation even after 33 days at room temperature before activating in water. Moreover, the PAA solutions prepared using the "All-in-One" composition showed high levels of sporicidal efficacy equivalent to the separate dry and liquid component formulations when assayed on contaminated sutures and porcelain penicylinders.

**[226]** Furthermore, it was found that the All-in-One composition can be "tuned" by varying the amount of sodium percarbonate used so as to generate PAA concentrations ranging from about 0.11% to 0.33%.

## EXAMPLE 10
## Use of Water Soluble Sachet for Delivery of An All-In-One PAA Generating Composition

**[227]** This example illustrates the preparation and use of an All-In-One composition for PAA generation formulated in a water-soluble sachet.

***Materials and Methods***

**[228]** Water soluble polyvinyl alcohol (PVA) sachets were obtained from Solupak Ltd. (Manchester, UK). Ten of these sachets were prepared for use with the All-In-One composition by filling each with 7.5 g of PGDA, 4.8 g of sodium percarbonate and 110 mg of the acyl transferase S54V-MsAcT. Each sachet was then sealed using a heat sealer.

**[229]** Sachets were shipped from the UK to the US, resulting in a transit time of 7 days before use. Upon receipt, a sachet was dissolved in 2000 mL of purified water (MilliQ) at 21°C. The pH and PAA concentration of the 2000 mL solution was measured at selected



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time points over 50 minute time course. PAA was assayed using the ABTS in citrate assay, as described above.

***Results***

**[230]** The sachet dissolved in the 2000 mL solution as expected delivering the All-In-One composition and resulting in the following PAA concentrations and pH values listed in Table 6.

**TABLE 6**

| Time (min) | PAA (wt. %) | pH |
|---|---|---|
| 0.00 | 0.02 | 5.20 |
| 5.00 | 0.02 | 10.10 |
| 10.00 | 0.04 | 10.19 |
| 15.00 | 0.08 | 9.78 |
| 20.00 | 0.12 | 9.37 |
| 25.00 | 0.14 | 8.97 |
| 30.00 | 0.16 | 8.62 |
| 50.00 | 0.18 | 8.12 |

**[231]** As shown above, the sachet delivery system performed as scaled. It generated the targeted PAA concentration and gave a typical pH profile, with a pH of 8.6 being generated at 20 minutes (the proposed dissolution time), which is a pH range generally considered as non-corrosive.

***Conclusions***

**[232]** The All-In-One composition is stable and can be delivered to solution effectively in a water soluble polyvinyl alcohol sachet. The resulting PAA concentrations and pH values of the solution after 30 minutes that are equivalent to those observed without the sachet.

**[233]** All patents and publications mentioned in the specification are indicative of the levels of those skilled in the art to which the invention pertains. All patents and publications are herein incorporated by reference to the same extent as if each individual publication was specifically and individually indicated to be incorporated by reference.

**[234]** Having described the preferred embodiments of the present invention, it will appear to those ordinarily skilled in the art that various modifications may be made to the disclosed embodiments, and that such modifications are intended to be within the scope of the present invention.

**[235]** Those of skill in the art readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned, as well as those



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inherent therein. The compositions and methods described herein are representative of preferred embodiments, are exemplary, and are not intended as limitations on the scope of the invention. It is readily apparent to one skilled in the art that varying substitutions and modifications may be made to the invention disclosed herein without departing from the scope and spirit of the invention.

**[236]** The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

**[237]** The invention has been described broadly and generically herein. Each of the narrower species and sub generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.



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## CLAIMS

I claim:

1. A composition comprising a perhydrolase enzyme, a hydrogen peroxide source, and an ester substrate, wherein said composition generates a peracid when mixed with water, and wherein said composition retains peracid generating activity for a time period of at least about 7 days.

2. The composition of claim 1, wherein the ester substrate is a liquid and the perhydrolase enzyme and hydrogen peroxide source are solids suspended in the liquid.

3. The composition of claim 1, wherein the peracid is selected from peracetic acid, pernonanoic acid, perpropionic acid, perbutanoic acid, perpentanoic acid, and perhexanoic acid.

4. The composition of claim 4, wherein the peracid is peracetic acid.

5. The composition of claim 1, wherein the ester substrate is propylene glycol diacetate.

6. The composition of claim 1, wherein the perhydrolase enzyme comprises the amino acid sequence set forth in SEQ ID NO:1.

7. The composition of claim 1, wherein the perhydrolase enzyme is the S54V variant of SEQ ID NO:1.

8. The composition of claim 1, wherein the hydrogen peroxide source is a hydrogen peroxide generating compound selected from sodium percarbonate, sodium perborate, and urea hydrogen peroxide.

9. The composition of claim 8, wherein the hydrogen peroxide source is sodium percarbonate.

10. The composition of claim 1, wherein the composition comprises about 0.001% to about 1% by weight perhydrolase enzyme, about 35% to about 45% by weight sodium percarbonate, and about 55% to about 65% by weight propylene glycol diacetate.



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11. The composition of claim 1, wherein the hydrogen peroxide source is an enzymatic hydrogen peroxide generation system comprising an oxidase and its substrate.

12. The composition of claim 11, wherein the oxidase is selected from glucose oxidase, sorbitol oxidase, hexose oxidase, choline oxidase, alcohol oxidase, glycerol oxidase, cholesterol oxidase, pyranose oxidase, carboxyalcohol oxidase, L-amino acid oxidase, glycine oxidase, pyruvate oxidase, glutamate oxidase, sarcosine oxidase, lysine oxidase, lactate oxidase, vanillyl oxidase, glycolate oxidase, galactose oxidase, uricase, oxalate oxidase, and xanthine oxidase.

13. The composition of claim 1, further comprising at least one additional enzyme selected from proteases, cellulases, amylases, and microbial cell wall degrading enzymes.

14. The composition of claim 1, wherein the composition further comprises at least one surfactant.

15. A method for preparing a decontamination solution comprising adding the composition of any of claims 1 to 14 to water and mixing for at least about 20 minutes.

16. A method for decontamination comprising:

(a) providing a composition according to any of claims 1 to 14;

(b) adding said composition to water and mixing, thereby generating an aqueous peracid solution;

(c) exposing an item comprising a contaminant to said solution.

17. The method of claim 16, wherein the composition is contained in a water soluble container.

18. The method of claim 18, wherein the container is a sachet made of polyvinyl alcohol film.

19. The method of claim 16, wherein the water is sterilized.

20. The method of claim 16, wherein said exposing comprises exposing said item to said solution at high temperature.



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21. The method of claim 16, wherein said contaminant comprises a toxin selected from botulinum toxin, anthracis toxin, ricin, scombroid toxin, ciguatoxin, tetrodotoxin, mycotoxins, and any combination thereof.

22. The method of claim 16, wherein said contaminant comprises a pathogen selected from bacteria, viruses, fungi, parasites, prions, and any combination thereof.

23. The method of claim 22, wherein said pathogen is selected *Bacillus spp., B. anthracis, Clostridium spp., C. botulinum, C. perfringens, Listeria spp., Staphylococcus spp., Streptococcus spp., Salmonella spp., Shigella ssp., E. coli, Yersinia spp., Y. pestis, Francisella spp., F. tularensis, Camplyobacter ssp., Vibrio spp., Brucella spp., Cryptosporidium spp., Giardia spp., Cyclospora spp.*, and *Trichinella spp.*

24. The method of claim 16, wherein said item is selected from hard surfaces, fabrics, food, feed, apparel, rugs, carpets, textiles, medical instruments, and veterinary instruments.

25. A system comprising a water soluble container comprising a stable composition according any of claims 1 to 15.

26. The system of claim 25, wherein said container is a sachet, ampoule, capsule, or sphere.

27. The system of claim 26, wherein the water soluble container is made of a water soluble polymer material polyvinyl alcohol, polyethylene oxides, cellulose derived water soluble carbohydrates, and polylactides.

28. A method for preparing a decontamination solution comprising adding system of claim 26 to water and mixing.

29. A kit for decontamination comprising the stable composition of any of claims 1 to 15 in packaging.

30. The kit of claim 29, wherein the composition is in a water soluble container.

31. The kit of claim 30, wherein the water soluble container is a sachet, ampoule, capsule, or sphere.



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32. The kit of claim 30, wherein the water soluble container is made of a water soluble polymer material selected from polyvinyl alcohol, polyethylene oxides, cellulose derived water soluble carbohydrates, and polylactides.

33. The kit of claim 29, further comprising an empty mixing container for mixing said composition with water.

34. The kit of claim 29, further comprising water in a sealed container, wherein the water is sterilized.

35. The kit of claim 29, further comprising instructions for use in a method according to claim 16.



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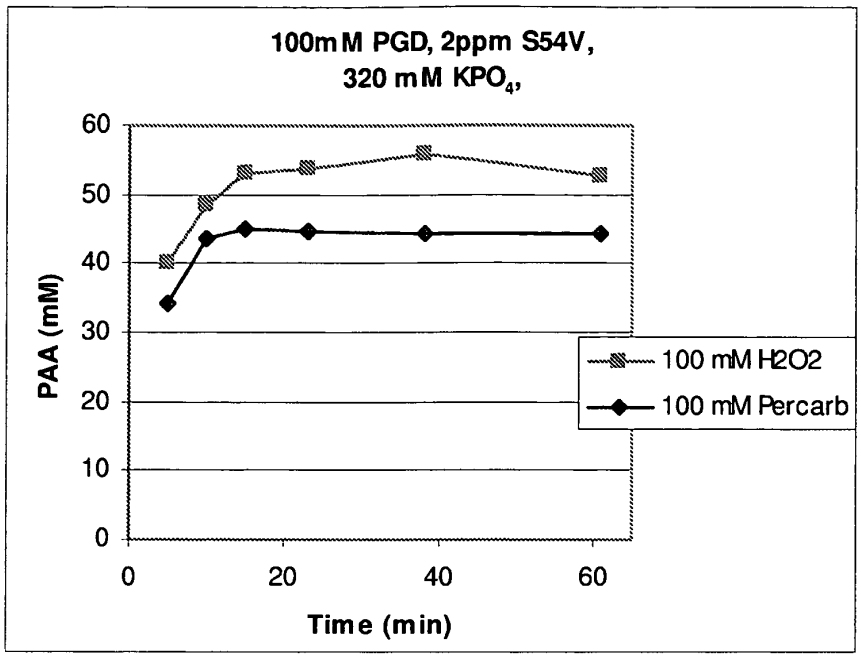

100mM PGD, 2ppm S54V,
320 mM KPO4,
PAA (mM)
Time (min)
100 mM H2O2
100 mM Percarb
0
10
20
30
40
50
60
0
20
40
60

FIG. 1

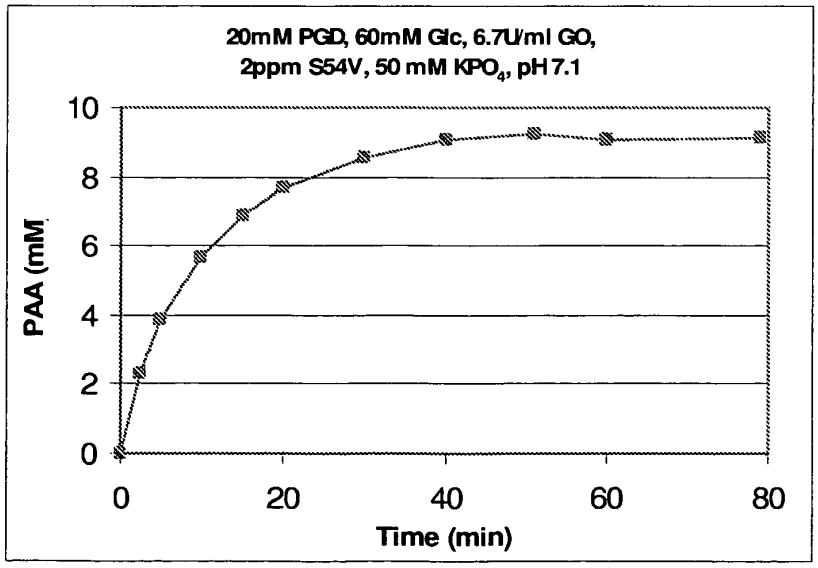

20mM PGD, 60mM Glc, 6.7U/ml GO,
2ppm S54V, 50 mM KPO4, pH 7.1
PAA (mM
Time (min)
0
2
4
6
8
10
0
20
40
60
80

FIG. 2

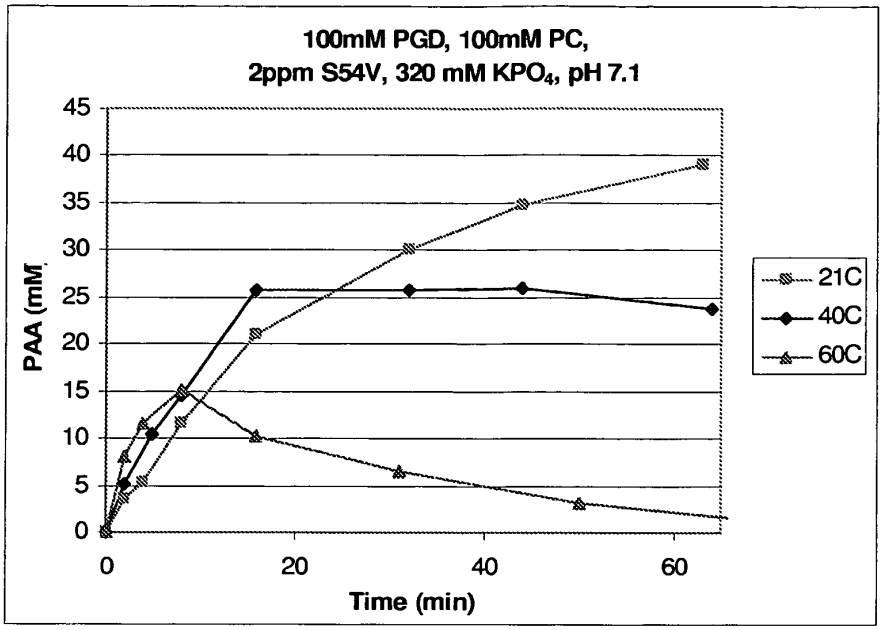

100mM PGD, 100mM PC,
2ppm S54V, 320 mM KPO4, pH 7.1
PAA (mM)
Time (min)
21C
40C
60C

FIG. 3

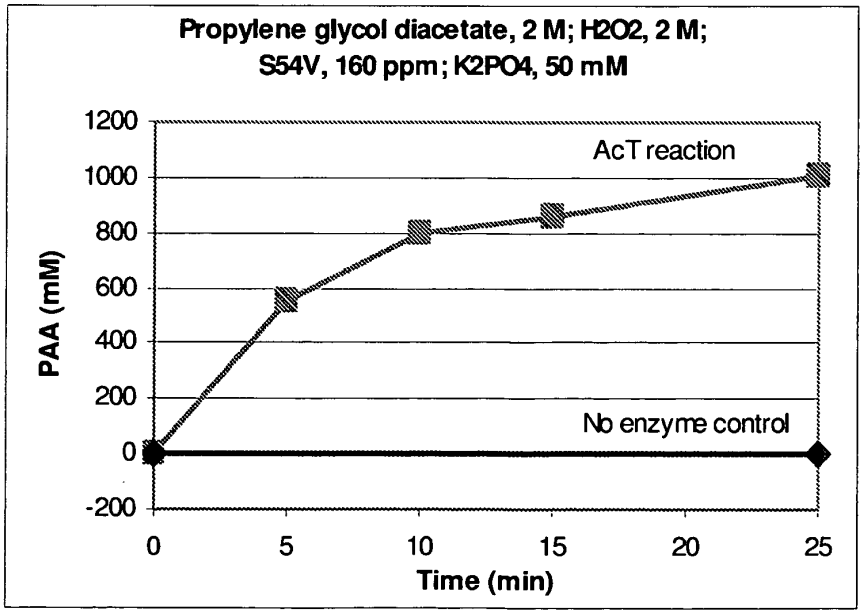

Propylene glycol diacetate, 2 M; H2O2, 2 M;
S54V, 160 ppm; K2PO4, 50 mM
PAA (mM)
Time (min)
AcT reaction
No enzyme control

FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/062633

A. CLASSIFICATION OF SUBJECT MATTER
INV. C12N9/16 C12N9/50 C12N9/52 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C12N

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, Sequence Search, EMBASE, BIOSIS, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 2005/056782 A (GENENCOR INT [US]; PROCTER & GAMBLE [US]; AMIN NEELAM S [US]; BOSTON M) 23 June 2005 (2005-06-23) Whole document, in particular p.33, 69-70, 72-73, 125, 134, 139, 155 | 1-35 |
| P,X | WO 2007/133263 A (GENENCOR INT [US]; CERVIN MARGUERITE A [US]; WHITED GREGG [US]) 22 November 2007 (2007-11-22) Whole document, in particular p.9, l.20-21 | 1-35 |
| X | WO 2007/044667 A (DU PONT [US]; DICOSIMO ROBERT [US]; PAYNE MARK S [US]; WAGNER LORRAINE) 19 April 2007 (2007-04-19) Whole document, in particular p.17-18 | 1-5,8-35 |

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 7 October 2008 | 20/10/2008 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Roscoe, Richard |

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## INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/062633

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 2006/119060 A (DU PONT [US]; DICOSIMO ROBERT [US]; PAYNE MARK SCOTT [US]; HANN EUGENI) 9 November 2006 (2006-11-09) Whole document, in particular p15, 26 | 1-5,8-35 |
| X | WO 2007/044666 A (DU PONT [US]; DICOSIMO ROBERT [US]; WAGNER LORRAINE [US]) 19 April 2007 (2007-04-19) Whole document, in particular p.13-14 | 1-5,8-35 |
| A | CARBONI-OERLEMANS C ET AL: "Hydrolase-catalysed synthesis of peroxycarboxylic acids: Biocatalytic promiscuity for practical applications" JOURNAL OF BIOTECHNOLOGY, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 126, no. 2, 1 November 2006 (2006-11-01), pages 140-151, XP002460370 ISSN: 0168-1656 the whole document | |
| A | NATTERMANN H ET AL: "Efficient killing of anthrax spores using aqueous and alcoholic peracetic acid solutions" BUNDESGESUNDHEITSBLATT GESUNDHEITSFORSCH.GESUNDHEITSSCHUTZ, SPRINGER, BERLIN, DE, vol. 48, no. 8, 1 August 2005 (2005-08-01), pages 939-950, XP019319123 ISSN: 1437-1588 the whole document | |

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2008/062633

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | EP 1954814 A2 | 13-08-2008 |
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| WO 2007044666 A | 19-04-2007 | EP 1941048 A2 | 09-07-2008 |

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*[Continued on next page]*

(54) Title: PRODUCTION OF PEROXYCARBOXYLIC ACIDS

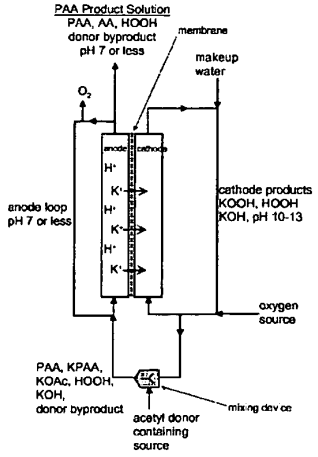



Fig. 5

(57) Abstract: Provided are various methods, systems and reactors for producing peroxycarboxylic acid compositions, such as non-equilibrium compositions of peracetic acid, for example. The methods and systems relate to electrolytic generation of hydrogen peroxide or peroxide ions in a reactor, wherein the generated materials are reacted with an acetyl donor to form peracetic acid. In an embodiment, a source of alkali metal ions is provided to an anode chamber such that the ratio of concentrations of the alkali metal ions to protons in the anode chamber of a reactor is greater than 1.

WO 2010/005607 A2

**Published**:

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# PRODUCTION OF PEROXYCARBOXYLIC ACIDS

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims the benefit of U.S. provisional application 61/037,821 filed March 19, 2008, which is incorporated by reference in its entirety herein to the extent not inconsistent with the disclosure herein.

## BACKGROUND OF THE INVENTION

**[0002]** Rapid, on-site production of peracetic acid (PAA) from safe, non-hazardous feedstocks is an enabling technology for facilities and applications where bulk storage and handling of hazardous materials is not permissible or where the consumption time exceeds the shelf life of bulk peracetic acid. Small quantity users of peracetic acid will especially benefit from on-site generation due to the impracticalities (hazardous and unstable) of distributing small quantities of peracetic acid.

**[0003]** Various methods for on-site peracetic acid production are known in the art. Disadvantages of such known methods are, among others, (1) the long reaction or cure times required to produce equilibrium concentrations of peracetic acid solutions; (2) costs of shipping, handling, and storage, (3) limited shelf life of concentrated acids, bases, and peroxides, which are all corrosives and hazardous materials; (4) cost of shipping large quantities of water containing merchant hydrogen peroxide; (5) the presence of stabilizers or contaminants originating from merchant hydrogen peroxide; (6) relatively low production rates or excessive equipment size and cost associated with direct electrochemical production of peracetic acid with gas diffusion electrode reactor technologies; (7) inability to recycle supporting electrolyte salts back into the production process. In addition, the practice of combining bulk chemical constituents obtained from merchant suppliers to produce non-equilibrium peroxycarboxylic acid solutions, including peracetic acid is incapable of producing the compositions provided herein. Processes and related devices provided herein eliminate these disadvantages and other disadvantages associated with shipping, storing and handling concentrated merchant peracetic acid.

**[0004]** U.S. Pat. Nos. 6,566,574, 6,723,890 and 7,271,137 all relate to compositions for neutralization or decontamination of chemical or biological toxins prepared by chemical mixing of various components including a reactive compound which can be hydrogen peroxide. U.S. Pat. No. 6,723,890 relates to an aqueous decontamination formulation comprising: a cationic surfactant; a cationic hydrotrope;



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certain reactive compounds (including hydrogen peroxide); a fatty alcohol having a concentration from greater than 1 wt. % to 2 wt %; and water. U.S. Pat. No. 7,271,137 relates to an aqueous decontamination formulation for use in disinfection and sterilization, consisting of (by weight percentage): 0.5-60% reactive compound selected from the group consisting of nucleophilic compounds and oxidizing compounds, which can be hydrogen peroxide; 1-10% water-soluble bleaching activator which can be monoacetin, diacetin, or triacetin, among other acetyl compounds, and; 3-30% of inorganic base which can comprise potassium acetate.

**[0005]** U.S. Pat. No.7,235,252, Preto et al. relates to a system for rapid preparation, just before use, of organic peroxyacids, in a hydroalcoholic environment, by mixing separately stored first and second reactants, where the first reactant includes an acyl donating group and the second reactant is in the solid state and comprises a peroxide anion source, a biocidal agent including at least one linear or branched aliphatic and/or aromatic alcohol, and a stabilizing buffer component suitable for keeping the second reactant at a desired pH value.

**[0006]** U.S. Pat. No. 5,505,740 (Kong et. al) describes a method for in-situ formation of peroxyacid using peroxyacid precursor, a source of hydrogen peroxide and a source for delayed release of acid for a bleaching product (wash solution) and a method of removing soil from fabrics. In the method of Kong et al. the aqueous wash solution is initially raised to a relatively high pH level (e.g., 9.5) to enhance production of the peroxyacid in the aqueous solution, followed by lowering the pH of the aqueous solution by, for example, the delayed release of acid, to enhance bleach performance. The source of the delayed release of acid may be an acid of delayed solubility, an acid coated with a low solubility agent or an acid generating species, or an acid independent of the bleaching product employed.

**[0007]** U.S. Pat. No. 5,122,538, Lokkesmoe et al, (Ecolab) relates to a process to generate peroxy acid sanitizing and bleaching compositions at the point-of-use. The process comprising introducing hydrogen peroxide and a carboxylic acid into a reactor and contacting the hydrogen peroxide and carboxylic acid in the presence of a sulfonic acid resin and in the substantial absence of active metal ions to form an aqueous peroxy acid composition at concentrations up to 20 wt %.

**[0008]** British Pat. Pub. No. GB 1,456,592 relates to a bleaching composition having both encapsulated bleaching granules and agglomerated pH-adjustment granules acid. The bleaching granules comprise an organic peroxy acid compound stabilized by salt(s) of strong acids and water of hydration, encapsulated in a fatty



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alcohol coating. The pH-adjustment granules comprise a water-soluble alkaline buffer yielding pH 7-9 agglomerated with a suitable adhesive material to yield the desired solubility delay. Preferred peroxyacid compounds are diperisophthalic acid, diperazelaic acid, diperadipic acid, monoperoxyisophthalic acid, monosodium salt of diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, p-nitroperoxy benzoic acid, and m-chloroperoxy benzoic acid.

**[0009]** U.S. Pat. No. 6,569,286 and published PCT No. WO0019006 (App. No. WO1999GB03178) relate to a process for bleaching of wood and non-wood pulp. In this process an agglomerate containing, among others, a bleach activator (e.g., tetraacetylethylenediamine, TAED) and a peroxide soluble binder (e.g., polyvinyl alcohol) is added to a dilute solution of hydrogen peroxide. The components are allowed to react and the pH of the resulting mixture is chemically adjusted to a suitable alkaline pH and the pulp is contacted with the resulting solution. The patent notes the use of an ion-selective barrier or membrane between the anodic and cathodic chambers of the electrolysis unit of Figure 1 therein. The barrier between the anodic and cathodic chambers in the device of Figure 1 is described as "a cation exchange membrane, which permits migration of protons ($H^+$) between the two chambers," and as a separation between electrolytes in the two chambers.

**[0010]** The above processes differ from the processes provided herein, at least in part, in that they are all based on mixing chemical precursors with no electrochemical production or electrochemical pH adjustment components.

**[0011]** Peracids can be produced in electrochemical cells or reactors by establishing a potential difference across electrodes immersed in electrically-conducting fluid and introducing appropriate reactant materials. For example, U.S. Pat. No. 6,387,238 (Merk et al.) (corresponding to WO 01/10215 or JP-T-2003-506120) relates to a method for preparing an antimicrobial solution containing peracetic acid in which hydrogen peroxide or peroxide ions are formed electrolytically and the hydrogen peroxide or peroxide ions are then reacted with an acetyl donor to form peracetic acid.

**[0012]** U.S. Pat. No. 6,949,178 (Tennakoon et al.) discloses a process and apparatus for the preparation of peroxyacetic acid at the cathode of an electrolytic cell having an ionically conducting membrane in intimate contact between an anode and a gas diffusion cathode. The method comprises supplying an aqueous organic acid solution to the anode, supplying a source of oxygen to the cathode, and generating peroxyacid at the cathode.



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**[0013]** European Patent EP1469102 (Ohsaka et al.) relates to a process and apparatus for electrolytically producing peracetic acid from acetic acid or acetate and an oxygen-containing gas using an electrolytic cell incorporating a gas diffusion electrode in the presence of a solid acid catalyst.

**[0014]** U.S. provisional application 61/019,825, filed Jan. 8, 2008 and U.S application 12/350,866, filed Jan. 8, 2009 relate to frozen non-equilibrium peroxycarboxylic acid compositions useful as antimicrobial ice.

## SUMMARY OF THE INVENTION

**[0015]** The invention provides improved methods of production of peroxycarboxylic acids and peroxycarboxylic acid containing solutions for various applications that utilize non-equilibrium peroxycarboxylic acids. The invention also provides improved compositions comprising peroxycarboxylic acids made by the methods herein.

**[0016]** In an embodiment, various processes for producing peroxycarboxylic acids, such as peracetic acid are provided. The production is particularly useful for on-site production of peracetic acid. Additionally, the peroxycarboxylic acid solutions produced, including peracetic acid solutions, have non-equilibrium compositions, such as characterized by high peroxycarboxylic acid (POA) and water to carboxylic acid (CA) and hydrogen peroxide ($H_2O_2$) ratios. In an aspect, the ratio of $[POA][H_2O]/[CA][H_2O_2]$ is $\geq 10$, $\geq 100$, $\geq 1000$, $\geq 10{,}000$. In another aspect the ratio of $[POA]:[H_2O_2]$ is: $\geq 1$, $\geq 5$, $\geq 10$, $\geq 100$, when the [POA]:[CA] concentration ratio is $\geq 1$.

**[0017]** More specifically, peracetic acid solutions of this invention have non-equilibrium compositions such as characterized by high peracetic acid (PAA) and water ($H_2O$) to acetic acid (AA) and hydrogen peroxide ($H_2O_2$) ratios. In an aspect, the ratio of $[PAA][H_2O]/[AA][H_2O_2]$ is $\geq 10$, $\geq 100$, $\geq 1000$, $\geq 10{,}000$. In another aspect the ratio of $[PAA]:[H_2O_2]$ is: $\geq 1$, $\geq 5$, $\geq 10$, $\geq 100$ when the [PAA]:[AA] concentration ratio is $\geq 1$. The non-equilibrium PAA solutions are economically competitive to equilibrium peracetic acid solutions commercially produced ("merchant") and having typically maximum weight peracetic acid content of between 5% and 35%, where $[PAA][H_2O]/[AA][H_2O_2]$ ratios are typically between 1.8 and 2.5.

**[0018]** A particular advantage of the use of non-equilibrium peroxycarboxylic acid is that solutions having concentrations of less than about 10 g/L peroxycarboxylic acid can be produced economically. This is particularly the case with non-equilibrium PAA. For example, making dilute solutions (<10 g/L) of equilibrium PAA is not cost-effective



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because in dilute solutions equilibrium favors the formation of hydrogen peroxide and acetic acid over PAA requiring high ratios of feed chemicals to obtain the desired PAA product at low concentration. Therefore, the cost of feed chemicals is much lower for non-equilibrium PAA relative to equilibrium PAA at low concentrations of PAA. Another advantage of non-equilibrium peroxycarboxylic acid is that the feed chemicals (hydrogen peroxide and acyl donor (or acetyl donor)) are significantly less hazardous than those of high concentration equilibrium solutions. This results in safer storage and handling for the end user.

**[0019]** In an aspect, processes disclosed herein utilize an electrochemical reactor that produces electrolytic hydrogen peroxide ($H_2O_2$) and/or peroxycarboxylic acid solutions of controlled pH and composition. Typical $H_2O_2$ concentrations of use in the process examples and made by various reactor systems include, but are not limited to, from 0.01% up to 0.1% (1000 mg/L), or from 0.01% up to 0.5% (5000 mg/L), or from 0.01% up to 5% (50,000 mg/L). Electrolytically produced peroxide solution is reacted with an acyl or acetyl donor to generate peroxycarboxylic acid. In an embodiment, the generated peroxycarboxylic acid is peracetic acid.

**[0020]** In an aspect, various processes are provided for producing peroxycarboxylic acids such as 2-hydroxyperbenzoic acid (peroxysalicylic acid) and other substituted derivatives of peroxybenzoic acids. The production is particularly useful for on-site production of peroxybenzoic acids. Additionally, produced peroxybenzoic acid solutions have non-equilibrium compositions such as characterized by high peroxybenzoic acid (PBA) and water ($H_2O$) to benzoic acid (BA) and hydrogen peroxide ($H_2O_2$) ratios. In an aspect, the ratio of $[PBA][H_2O]/[BA][H_2O_2]$ is $\geq 10$, $\geq 100$, $\geq 1000$, $\geq 10{,}000$, thus making them economically competitive to commercial peroxybenzoic acid sources, while eliminating the hazards and costs of shipping and storing organic peroxides such as peroxybenzoic acids. In specific embodiments, solutions of peroxycarboxylic acids of this invention are solutions in water. In other specific embodiments, solutions of peroxycarboxylic acids are solutions in aqueous solvents which are mixtures of water and a water miscible organic solvent, such as a lower alcohol, and in particular ethanol. In an aspect, processes disclosed herein utilize an electrochemical reactor that produces electrolytic hydrogen peroxide ($H_2O_2$) solutions of controlled pH and composition. Typical $H_2O_2$ concentrations of use in the process examples and made by various reactor systems include, but are not limited to, from 0.01% up to 0.1% (1000 mg/L), or from 0.01% up to 0.5% (5000 mg/L), or from 0.01% up to 5% (50,000 mg/L). Electrolytically produced peroxide solution is reacted with an



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acyl donor, such as 2-hydroxybenzoic acid ethyl ester (salicylic acid ethyl ester, ethyl salicylate), to generate peroxybenzoic acids. In an embodiment, the generated peroxycarboxylic acid is peroxysalicylic acid.

**[0021]** In an aspect, the acyl or acetyl donor is not in contact with an electrode of the reactor. Instead, the donor is placed in a chamber that does not contain an electrode. Examples of such chambers include, but are not limited to, a chamber that is external to the reactor and a chamber that is internal to the reactor, but is not in direct fluid contact with the electrodes. In this aspect, "not in direct fluid contact" refers to membranes that separate the central chamber from each of the cathode and anode chambers so that the central chamber contains "post-processed" peroxycarboxylixc acid product. Such systems provide a number of benefits, such as not electrolyzing the acyl or acetyl donor, POA or PAA product or $H_2O_2$ to inactive forms, improved process monitoring and process control, thereby achieving higher yields and reliability compared to conventional electrochemical POA (particularly PAA) production. Additional advantages include, but are not limited to, preserving the as-formed [POA]:[$H_2O_2$] ratio, access to the acyl or acetyl donor(s), POA or PAA components and mixture for monitoring and replenishing as necessary, and ability to reliably control end product characteristics.

**[0022]** In an aspect, the acyl or acetyl donor is not in contact with a cathode of the reactor. For example, the donor is placed in a chamber that contains an anode. Such a system provides the benefits of not electrolyzing the POA or PAA product to inactive forms, improved process monitoring and process control, thereby achieving higher yields and reliability compared to conventional electrochemical POA or PAA production. Additional advantages include, but are not limited to, increasing the [POA]:[$H_2O_2$] ratio, reducing concentration of acyl or acetyl donor byproduct, and ability to reliably control end product characteristics.

**[0023]** The peracid production rate and yield amount depends on the reactor system and operating conditions including, but not limited to, concentration of reactants, temperature, pH, reactor materials such as membranes, electrodes, operating voltage, electrolyte composition and concentration, added chemical stabilizers, flow-rates, delivery rate and mechanism of supply of oxygen-containing gas, etc. The process may be operated in batch mode. The process may be operated in continuous mode. The process may be semi-batch or semi-continuous mode. Generated peroxycarboxylic acid-containing solutions are pH adjusted by either chemical and/or electrolytic methods, the latter allowing electrolyte ions to be recovered back into the electrolytic



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peroxide production process, thereby facilitating continuous or semi-continuous operating modes. The pH adjustment may be automatic or semi-automated such as by feedback control and flowloops where caustic flow-stream output may be at least partially introduced into a feedstock stream.

**[0024]** The peroxycarboxylic acid product solution produced by any of these processes can be formed very rapidly and on-demand with non-equilibrium compositions making it more convenient, efficient, and cost effective while being safer to handle at relatively low (point of use) concentrations compared to concentrated peroxycarboxylic acid products having equilibrium compositions.

**[0025]** In an embodiment, the processes and device systems for performing the processes provide one or more of: (1) Electrochemical production of a caustic hydrogen peroxide solution where the solution pH, concentration of peroxide, and ratio of hydroxide to peroxide are controlled by the electrolytic reactor process by flowstream manipulation, residence time, mixing methods, ion selection and concentration, and other parameter control as known in the art; (2) Reaction of the electrolytic caustic hydrogen peroxide solution with an acyl or acetyl donor to rapidly produce non-equilibrium peroxycarboxylic acid solutions that may optionally include additional additives (such as electrolytes, stabilizers, buffers, alcohols, etc.); (3) The pH of the resulting peroxycarboxylic acid solution, particularly peracetic acid, may optionally be adjusted to lower pH (including, but not limited to $pH \leq 7$, $pH \leq 6$, or $1.5 \leq pH \leq 4.5$) by either a chemical means of mixing acid with the solutions or electrolytically adjusting the pH in the same apparatus used to produce the electrolytic caustic hydrogen peroxide solution (e.g., and optionally a combination of the two pH adjustment methods); (4) Recovery of electrolyte cations liberated during pH adjustment of the peroxycarboxylic acid solutions for recycle of electrolyte cations back into the electrolytic caustic hydrogen peroxide production process; (5) Feedstocks for this process are electricity, an oxygen-containing gas, water, an electrolyte salt, and an acyl or acetyl donor.

**[0026]** There are a large number of known acyl or acetyl donors including, but not limited to, diacetin, triacetin, acetylsalicylic acid, tetraacetylethylenediamine. In an aspect, the acyl donor is not a carboxylic acid, but instead is a donor that provides for a non-reversible chemical reaction with hydrogen peroxide to form the corresponding peroxycarboxylic acid. In a more specific aspect, the acetyl donor is not acetic acid, but instead is a donor that provides for a non-reversible chemical reaction with hydrogen peroxide to form peracetic acid. The reaction between the acetyl donor and hydrogen peroxide is accelerated at alkaline pH, and in some embodiments, preferably between



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$10 \leq pH \leq 13$. The acetyl donor or mixture of donors may be in liquid or solid form or dissolved in a solvent when reacted with a solution of hydrogen peroxide, preferably at alkaline pH, to form peracetic acid. The resulting peracetic acid product may then be used as made or its pH adjusted to a desirable level. Additionally, a peroxide stabilizer may be added before, during, or after combination of the acetyl donor with hydrogen peroxide.

**[0027]** In an embodiment, the electrochemically produced caustic hydrogen peroxide solution is chemically reacted with an acyl or acetyl donor (and other additives if desired). Next, the pH of the resulting peroxycarboxylic acid solution is adjusted electrolytically and/or chemically if desired (for product stabilization or pH requirements of the end use application). During the electrolytic product pH adjustment process or after chemical pH adjustment, the cations liberated by neutralization of caustic are electrolytically separated and recovered back into the electrochemical caustic hydrogen peroxide production process. This electrolytic recycling of cations reduces or eliminates the need for additional electrolyte salt feedstock. The operating conditions of the electrochemical process are also adjusted to optimize the caustic hydrogen peroxide solution pH and hydroxide to peroxide ratio prior to reaction with the acyl or acetyl donor, whereby the chemical reaction rate and yield of peroxycarboxylic acid is maximized. Depending on the specific reactor and system, parameters of interest include return flow-rates of feedback loops, residence time in mixing or reactor chambers, electrolyte concentrations, any one or more feedstock parameters or compositions, including electrolytes, stabilizers, co-solvents, pH adjusters, pH buffers.

**[0028]** In another embodiment, sequential physical mixing of bulk chemicals is used to generate peroxycarboxylic acid in situ. This alternative physical mixing approach includes the steps of (1) mixing a base with hydrogen peroxide to produce a caustic peroxide solution; (2) mixing the caustic peroxide solution with an acyl donor (e.g. an acetyl donor) to produce a non-equilibrium peroxycarboxylic acid solution; (3) adjusting the pH of the resulting peroxycarboxylic acid solution with acid (for product stabilization or pH requirements of the end use application). The required feedstocks for this process in an automated system are electricity, water, merchant hydrogen peroxide, base (such as sodium or potassium hydroxide or acetate), acyl donors (e.g., acetyl donors), and acid (such as sulfuric or acetic acid).

**[0029]** In an embodiment, the invention is an electrolytic reactor for carrying out any of the processes disclosed herein. Depending on the particular process, the reactor may be a two-chamber or a three-chamber reactor. In an aspect, a mixing chamber is



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integrated within the reactor for mixing an acyl donor (e.g., an acetyl donor) with a caustic hydrogen peroxide solution, wherein the chamber is electrically isolated from the cathode and anode. In an aspect, the reactor and process provides PAA production without a need for distillation. As required, various flowloops for introducing feedstock, feedback lines for pH control, and output lines for collecting POA (e.g., PAA) product solution are incorporated.

**[0030]** In another embodiment, provided is a method for making a peroxycarboxylic acid composition by electrolytically generating alkaline hydrogen peroxide or peroxide ions in a reactor comprising a cathode chamber having a cathode, an anode chamber having an anode and at least one cation exchange membrane separating said chambers. A source of alkali metal ions is provided to the anode chamber such that the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than 1 and the predominant cations transported through the at least one cation exchange membrane are alkali metal ions. Hydrogen peroxide or peroxide ions are reacted with an acetyl donor to form peracetic acid in a mixing chamber that is electrically isolated from the anode and cathode of the reactor to produce the peroxycarboxylic acid composition comprising alkali metal ions.

**[0031]** In an aspect, the source of alkali metal ions is a salt added to said anode chamber, or is the peroxycarboxylic acid composition formed in the method, wherein at least a portion of the composition is recycled to the anode chamber.

**[0032]** In another aspect, any of the methods provided herein relate to the source of alkali metal ions being added directly to the anode chamber.

**[0033]** In an embodiment, any of the methods provided herein use a two chamber reactor, such as an anode chamber and a cathode chamber. In an embodiment, any of the methods provided herein use a reactor comprising a central chamber between the anode and cathode chambers and separated from each of the chambers by at least one cation exchange membrane and the source of alkali metal ions is added to the anode chamber, the central chamber or both. Optionally, the alkaline hydrogen peroxide or peroxide ions has a pH greater than or equal to 10 and less than or equal to 13.

**[0034]** Any of the methods provided herein optionally have an alkaline hydrogen peroxide or peroxide ions with a pH greater than or equal to 10 and less than or equal to 13.

**[0035]** In another aspect, any of the methods provided herein relate to a reacting step that further comprises introducing one or more acetyl donors to the mixing chamber; and introducing the electrolytically generated alkaline hydrogen peroxide or



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peroxide ions from a cathode chamber of the reactor to the mixing chamber, thereby generating the peracetic acid composition. Any of the methods provided herein further comprise introducing to the reactor a peroxide stabilizer, an electrolyte salt or both. In an aspect, any of the methods provided herein relate to a peroxycarboxylic acid composition formed having a pH that is less than or equal to 8.

**[0036]** Further provided are methods related to specific ratio of concentrations, such as molar ratios, of alkali metal ions to protons formed in the anode chamber. In an aspect, provided are ratios in the anode chamber that are greater than or equal to 3; between about 3 and 4, inclusive; and greater than or equal to 10, for example.

**[0037]** In another embodiment, any of the methods provided herein further comprise introducing the peroxycarboxylic acid composition from the mixing chamber to the reactor, adjusting the pH of the peroxycarboxylic acid composition by electrodialysis, and removing the peroxycarboxylic acid composition from the reactor to obtain a peroxycarboxylic acid product solution, wherein the peroxycarboxylic acid product solution has a pH that is less than or equal 8, and optionally wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than or equal to 3, or greater than or equal to 10.

**[0038]** Also provided are methods for making a peroxycarboxylic acid composition by electrolytically generating hydrogen peroxide or peroxide ions in an electrochemical reactor having an anode chamber having an anode and a cathode chamber having a cathode and at least one cation exchange membrane separating the anode and cathode chambers. Hydrogen peroxide or peroxide ions are reacted with an acyl or acetyl donor to form peroxycarboxylic acid, wherein the peroxycarboxylic acid is formed in a mixing chamber that is electrically isolated from the anode and cathode. A salt is introduced into the reactor and an alkaline electrolyte solution produced by electrodialysis of the salt introduced to the reactor. The alkaline caustic electrolyte solution adjusts the pH of the hydrogen peroxide or peroxide ions to a pH that is greater than or equal to 9.5 and less than or equal to 13.

**[0039]** In an aspect, the method further comprises adding a source of alkali metal cations to an anode chamber of the reactor. In an embodiment of this aspect, the ratio of concentrations of alkali metal ions to protons in the anode chamber is greater than or equal to 1; greater than or equal to 3, greater than or equal to 3 and less than or equal to 4; or greater than or equal to 10.

**[0040]** In another aspect, the reactor has a catholyte solution containing the generated hydrogen peroxide or peroxide ions, and the method further comprises,



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controlling the reactor catholyte pH, wherein the catholyte pH is greater than or equal to 10 and less than or equal to 13; and/or controlling a peroxide to hydroxide ratio in the catholyte solution, wherein the ratio is greater than or equal to 0.5:1 and less than or equal to 5:1 or between about 0.5:1 and 2:1. Optionally, the controlling steps comprise balancing transfer rates of alkali metal cations and acid protons introduced to the catholyte solution.

**[0041]** In an aspect, the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than 1, the alkaline hydrogen peroxide or peroxide ions has a pH greater than or equal to 10 and less than or equal to 13, and the peroxycarboxylic acid composition has a pH less than or equal to 8.

**[0042]** In another aspect, the peroxycarboxylic acid composition is introduced to an anode chamber of the reactor, thereby lowering said peracetic acid composition pH by electrodialysis and lowering the hydrogen peroxide concentration.

**[0043]** Any of the methods provided herein further comprise introducing at least a portion of the peroxycarboxylic acid composition from the anode chamber to the mixing chamber by an acidic anolyte loop, thereby providing additional pH regulation of the peroxycarboxylic acid composition.

**[0044]** In an aspect, any of the methods relate to a peroxycarboxylic acid that is peracetic acid. In another aspect, any of the methods relate to a peroxycarboxylic acid that is a substituted derivative of peroxybenzoic acid. In another aspect, any of the methods are for making a peroxycarboxylic acid that is a non-equilibrium composition.

**[0045]** Also provided is an electrochemical reactor for generating peroxycarboxylic acid compositions, comprising an anode positioned within an anode chamber; a cathode positioned within a cathode chamber for producing alkaline hydrogen peroxide catholyte solution; at least one cation exchange membrane separating the anode and cathode chambers; an optional central chamber between the cathode and anode chambers and separated from each of the chambers by at least one cation exchange membrane; a mixing chamber electrically isolated from the anode and cathode for receiving an acyl donor; a mixing chamber conduit for supplying a caustic catholyte solution to the mixing chamber; a peroxycarboxylic acid (POA) composition conduit for introducing POA made in the mixing chamber to the reactor, wherein the POA composition conduit is operably connected to the anode chamber or the optional central chamber; and a reactor outlet for removing from the reactor at least a portion of the POA formed in the reactor. In an embodiment, the removed POA is in a solution of lower pH than the POA made in the mixing chamber



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**[0046]** In an aspect, the reactor further comprises an acidic anolyte loop that operably connects the reactor outlet to the POA composition conduit, thereby providing rapid pH adjustment to the POA made in said mixing chamber. In another aspect, the mixing chamber is positioned either external to the reactor or internal to the reactor.

**[0047]** Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles relating to the invention. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0048]** **FIG. 1** is a flow-chart summary of one embodiment of a PAA-producing process, where produced PAA is fed into the reactor, such as into a central chamber (for a three-chamber reactor) or anode chamber (for a two-chamber reactor).

**[0049]** **FIG. 2** is a flow-chart summary of one embodiment of a PAA-producing process, where produced PAA is not fed into the reactor, but instead is used directly such as for caustic applications like. A base-containing source or acid-containing source may be used as desired to control the output PAA pH.

**[0050]** **FIG. 3** is a schematic illustration of a three-chamber electrolytic reactor for peracetic acid generation.

**[0051]** **FIG. 4** is a schematic illustration of a two-chamber electrolytic reactor for peracetic acid generation, wherein the generated peracetic acid is passed over the anode as anolyte solution to shift pH from caustic to acid.

**[0052]** **FIG. 5** is a schematic illustration of a two-chamber electrolytic reactor for peracetic acid generation, wherein the generated peracetic acid is dosed into an acidic anolyte loop to rapidly shift the pH from caustic to acid.

**[0053]** **FIG. 6** is a schematic illustration of a two-chamber electrolytic reactor for peracetic acid generation, wherein the generated peracetic acid is directly isolated or used without subsequent interaction with the reactor.

**[0054]** **Fig. 7** is a schematic diagram of preferred dosing and mixing of materials in generator process, excluding the electrolytic reactor.

**[0055]** **Fig. 8** is a graph of concentration of peracetic acid with time to determine the degradation rate in the absence of peroxide stabilizers. The average half life of the peracetic acid in the product solution was 10 days. The decay curve was approximately linear. See Example 10.



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**[0056]** **Fig. 9** is a graph of concentration of peracetic acid to determine the degradation rate in the absence of peroxide stabilizers. The average half life of the peracetic acid in the solutions was 1.8 hours. The decay curve was approximately linear as illustrated.

## DETAILED DESCRIPTION OF THE INVENTION

**[0057]** "Acyl donor" refers to a material which supplies an acyl donor for reacting with the hydrogen peroxide or peroxide ions to form a solution which includes a peroxycarboxylic acid. In a specific embodiment, an "acyl donor" refers to a material which supplies an acetyl donor for reacting with the hydrogen peroxide or peroxide ions to form a solution which includes peracetic acid.

**[0058]** "Acetyl donor" refers to a material which supplies an acetyl donor for reacting with the hydrogen peroxide or peroxide ions to form a solution which includes peracetic acid. The composition of the acetyl donor source for use in a commercial reactor system may be composed of an acetyl donor compound, optionally containing more than one type of acetyl donor compound, optionally containing an electrolyte salt, optionally containing a peroxide stabilizer, optionally containing a base, optionally containing an acid, optionally containing a solvent (water, alcohols, organic). Examples of acetyl donors include, but are not limited to O-acetyl donors (--O--$C(O)CH_3$), such as acetin, diacetin, triacetin, acetylsalicylic acid, (β)-D-glucose pentaacetate, cellulose (mono and tri) acetate, D-mannitol hexaacetate, sucrose octaacetate, and acetic anhydride. N-acetyl donors (--N--$C(O)CH_3$) may also be used, such as N,N,N'N'-tetraacetylethylenediamine (TAED), N-acetyl glycine, N-acetyl-DL-methionine, 6-acetamidohexanoic acid, N-acetyl-L-cysteine, 4-acetamidophenol, and N-acetyl-L-glutamine. Examples of acyl donors

**[0059]** "Peroxycarboxylic acids" (POA, also referred to in the art as peracids, peroxyacids, or percarboxylic acids) include, but are not limited to, peracetic acid (peroxyacetic acid), peroxybenzoic acid (perbenzoic acid) and substituted forms of peroxybenzoic acid; di-peroxymalonic acid, di-peroxysuccinic acid, di-peroxyglutaric acid, di-peroxyadipic acid; all isomeric forms of each of peroxypropionic acid, peroxybutanoic acid, peroxyhexanoic acid, peroxydodecanoic acid, and peroxylactic acid; and peroxycarboxylic acid derivatives of amides, carbohydrates, saccharides, polysaccharides, cellulose, fatty acids and surfactants. Peroxyacetic acid (PAA) is a representative peroxycarboxylic acid (POA). Methods and compositions herein which



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are exemplified with PAA can be practiced in general with any one or more peroxycarboxylic acids (POA).

**[0060]** "POA composition" or more specifically 'PAA composition" refers to the POA, or more specifically the PAA, made and released from the mixing chamber. "POA product solution" or more specifically "PAA product solution" refers to POA, or more specifically PAA, removed from the reactor, such as a POA or PAA composition that has been introduced to the reactor. In an embodiment, the POA product solution has a pH that is lower than the POA composition that is introduced to the reactor. In an aspect the POA product solution, specifically the PAA product solution has a pH ≤ 8, pH ≤ 7, pH ≤ 6, or 1.5 ≤ pH ≤ 4.5.

**[0061]** "Reactor" refers to an electrolytic chamber that uses electricity, water and oxygen to generate a reactant such as hydrogen peroxide for producing PAA. Suitable reactors are known in the art (see, e.g., U.S. Pat. Nos. 6,387,238, 6,949,178; U.S. Pub. No. 2007/0074975, each of which are hereby incorporated by reference, such as for reactor design and materials) and are disclosed herein. Some common features of such reactors are outlined in **FIGs. 3-6** and include electrodes and electrode-containing chambers, membranes, inputs for reactants, and a power supply.

**[0062]** "Not in contact" refers to a reactant material that is placed in a chamber that is isolated from the electrode (cathode and anode) chambers, such as a mixing chamber. In processes disclosed herein, this refers to acetyl donors in a mixing chamber that is physically separated from the electrode chambers.

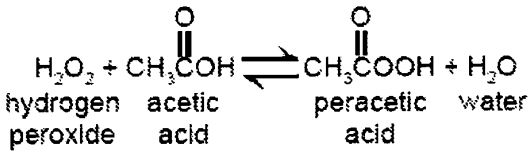
**[0063]** "Caustic" refers to basic pH solutions. In an aspect the pH is greater than about 9, greater than 10, or greater than and equal to 10 and less than and equal to 13. In an aspect, the hydrogen peroxide-containing catholyte solution is caustic, such as pH ≥ 9, pH ≥ 10, or 9.5 ≤ pH ≤ 13 and is introduced to the acetyl donor containing source to generate PAA.

**[0064]** "Equilibrium" and "non-equilibrium". "Equilibrium PAA" is most commonly produced by mixing hydrogen peroxide, acetic acid, water and an acid catalyst. The mixture is allowed to "cure" for several days at which time the mixture reaches steady state equilibrium.

**[0065]** In aqueous solution peracetic acid is in a chemical equilibrium with acetic acid, hydrogen peroxide and water. This equilibrium is represented in the following Equation (1):



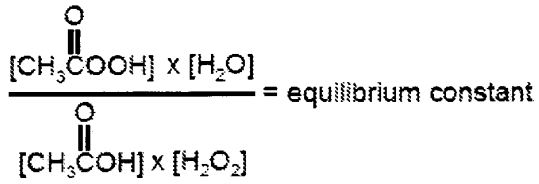
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(1)

**[0066]** For example, a higher concentration of reactants is required to produce a higher concentration of peracetic acid. Conversely, a higher concentration of water will drive the reaction backwards, which means dilute solutions have very low peracetic acid equilibrium concentrations and mostly contain water and unused starting materials.

**[0067]** The molar concentration ratio of products versus reactants gives an equilibrium ratio often referred to as the equilibrium constant as shown in the following Equation (2A):




(2A)

**[0068]** For equilibrium peracetic acid solutions this equilibrium constant typically ranges between 1.8 and 2.5. [See "Organic Peroxides," Daniel Swern, Editor; Wiley-Interscience, New York, 1970-72 (3 volume series)]. As used herein, in certain aspects "nonequilibrium peracetic acid solutions" refer to PAA solutions having equilibrium constants greater than 10, greater than 100, greater than 1000, and greater than 10,000. Equilibrium solutions of peroxycarboxylic other than peracetic acid are known in the art and equilibrium constants for the generic equilibrium equation:

$$\frac{[RCO\text{-}O\text{-}OH] \times [H_2O]}{[RCO\text{-}OH] \times [H_2O_2]} = \text{equilibrium constant} \qquad (2B)$$

are known in the art or can be determined by methods well-known in the art.

An example of typical equilibrium compositions commercially produced and distributed in bulk is 5-35% by weight peracetic acid, up to 30% hydrogen peroxide, up to 40% acetic acid and the balance being water. The weight ratio of hydrogen peroxide to peracetic acid to acetic acid in the merchant products ranges between 4.6:1:1.3 (5-6% PAA equilibrium product) and 1:5.4:6.2 (35% PAA equilibrium product). Using only the $[H_2O_2]$:[PAA] ratio is an oversimplified definition for distinguishing equilibrium from non-equilibrium peracetic acid solutions in that it does not represent the acetic acid constituent involved with the equilibrium constant.



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"Non-equilibrium" refers to chemical mixtures that do not provide an equilibrium constant value, such as provided by Equation (2A) for peracetic acid solutions, that is between about 1.8 and 2.5 or for Equation (2B) where the specific equilibrium constant depends upon the R group. Accordingly, a non-equilibrium PAA solution is optionally described as having an equilibrium constant typically as calculated by Equation (2) that is not between 1.8 and 2.5. In an aspect, the nonequilibrium PAA is defined as those solutions having an equilibrium constant of greater than 10, greater than 100, greater than 1000, and greater than 10,000.

**[0069]** In specific embodiments, herein the non-equilibrium PAA solutions include those in which the ratio of hydrogen peroxide to PAA is less than 2, those in which this ratio is less than 1 and to those in which this ratio is 0.5 or less. Non-equilibrium PAA solutions of this invention include those in which the concentration of PAA is less than 200 mg/L, those in which this concentration is 100 mg/L or less, those in which the concentration is 50 mg/L or less, those in which the concentration is 10 mg/L or less and those in which the concentration is 5 mg/L or less.

**[0070]** Current practice in cleaning, disinfection and water treatment applications is distribution of bulk PAA solutions delivered and stored in vented drums until use. This is typically sold as equilibrium solutions with PAA concentrations of 5-6%, 15% or 35% in the presence of excess hydrogen peroxide and acetic acid with water making up the balance.

**[0071]** Alternatively, large quantities of equilibrium PAA can be produced on-site by blending concentrated hydrogen peroxide and acetic acid in water. Sulfuric acid may also be added as a catalyst to accelerate the equilibration. The blended solution is allowed to 'cure' for at least 6-10 days while reaching chemical equilibrium prior to use. The cure time increases with decreasing concentration of either starting material and is several weeks or longer at very low point-of-use concentrations. Most applications using peracetic acid (with the exception of pulp bleaching) are regulated to use less than 170 mg/L concentrations for hard surface cleaning and less than 80 mg/L for contact with produce and often less than 10 mg/L for water treatment.

**[0072]** As an example of the drawback to producing low concentration equilibrium solutions, a 200 mg/L concentration of peracetic acid in an equilibrium solution would contain 4000 mg/L hydrogen peroxide and 35,000 mg/L acetic acid that is unused starting material (equilibrium constant = 2.05). In contrast, non-equilibrium peracetic acid solutions can contain 200 mg/L peracetic acid, 200 mg/L hydrogen peroxide and 160 mg/L acetic acid (equilibrium constant = 9315). Therefore to directly produce low



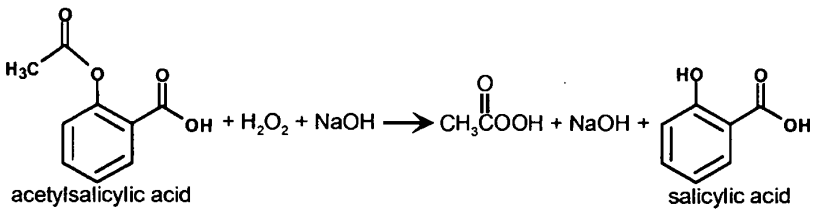
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concentrations of peracetic acid rapidly and economically on-site, a non-equilibrium product is required.

**[0073]** Conventional non-equilibrium peracetic acid solutions are commercially produced in bulk by distillation of equilibrium peracetic acid solutions and storing the non-equilibrium distillate near its freezing point to minimize decomposition and re-equilibration during storage. Equilibrium peracetic acid solutions are produced by reacting concentrated hydrogen peroxide with concentrated acetic acid in a 1-20% sulfuric acid solution where the sulfuric acid acts as an acid catalyst to make the reaction occur rapidly. The non-equilibrium peracetic acid produced is distilled from the reaction mixture and stored near its freezing point to minimize decomposition. This method of producing non-equilibrium peracetic acid is not practical for smaller users due to the operating skill required for such a production process, the use of concentrated hazardous materials, and the explosion hazard created by distillation of concentrated peroxides.

**[0074]** Alternatively, non-equilibrium peracetic acid solutions can be chemically produced by an irreversible, non-equilibrium reaction of hydrogen peroxide with an acetyl donor in a solvent such as, but not limited to, water. One typical example of this reaction using acetylsalicylic acid as the acetyl donor is given in Equation (3). Typically caustic pH (pH >10) is used to accelerate the reaction since the hydrogen peroxide anion is a much better nucleophile than hydrogen peroxide. The reaction pH can be adjusted with an appropriate base (proton acceptors such as hydroxide or amines for example).

**[0075]** Both the hydrogen peroxide anion and hydroxide anion compete in the reaction with the acetyl donor, the former producing peracetic acid and the latter producing acetic acid. The percent conversion of the acetyl donor to peracetic acid is maximized by optimizing the hydrogen peroxide to hydroxide ratio mixing method and reaction time. In embodiments, the processes provided herein adjust the hydrogen peroxide to hydroxide ratio, such as ratios of 1:2, 1:1.5, 1:1, 1.5:1, 2:1, greater than 2:1. In the example given below, up to 85% of the acetyl donor is converted to peracetic acid.

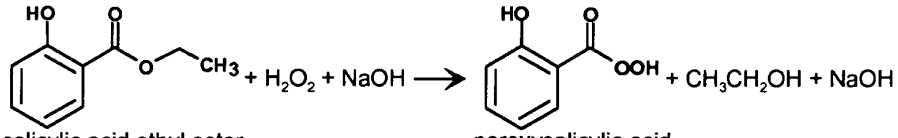



acetylsalicylic acid salicylic acid (3)



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**[0076]** Both the hydrogen peroxide anion and hydroxide anion compete in the reaction with the acyl donor, the former producing a peroxycarboxylic acid and the latter producing a carboxylic acid. The percent conversion of the acyl donor to peroxycarboxylic acid is maximized by optimizing the hydrogen peroxide to hydroxide ratio, mixing method and reaction time. In embodiments, the processes provided herein adjust the hydrogen peroxide to hydroxide ratio, such as ratios of 1:2, 1:1.5, 1:1, 1.5:1, 2:1, greater than 2:1. In the example given below, up to 85% of the acyl donor, salicylic acid ethyl ester, is converted to a peroxycarboxylic acid and preferably greater than 85% of the acyl donor is converted to peroxycarboxylic acid. In the example given below, the peroxysalicylic acid may be used, for example, as a biocide, an epoxidation agent for alkenes, or a polymerization agent, catalyst or initiator. In the example given below, the acyl donor byproduct is ethanol, which may be used as a co-solvent component or biocidal component of a product solution.




salicylic acid ethyl ester peroxysalicylic acid (3.5)

**[0077]** An example of a non-equilibrium reaction solution in the above Equation (3) is combining 1.1 g/L hydrogen peroxide adjusted to pH 12.0 with sodium hydroxide and reacted with 10 g/L acetylsalicylic acid. The product solution contains 0.32 g/L hydrogen peroxide and 1.9 g/L peracetic acid with 85% conversion of the acetylsalicylic acid. This product has a non-equilibrium hydrogen peroxide to peracetic acid ratio of 0.17, more than ten times lower than for merchant equilibrium products.

**[0078]** At alkaline pH (pH >7.5), the peracetic acid is unstable and decomposes to oxygen and acetic acid and/or acetate anion over time at a much higher rate than at lower pH. Alternatively, the acetyl donor byproduct may further react with the peracetic acid in the presence of alkaline pH causing its decomposition or consumption with acetic acid and oxygen as the byproducts. Therefore, the adjustment of the pH to neutral (pH 7) or acidic (pH <7) is often desired for stabilization and storage.

**[0079]** At alkaline pH ($7.5 \leq pH \leq 10.5$), near the pKa of peracetic acid (pKa = 8.2), peracetic acid is least stable. Decomposition of peracetic acid is greatly accelerated in this pH range due to a self reaction between the protonated and deprotonated (anion) forms of peracetic acid leading to the evolution of oxygen. The electronic state of oxygen evolved by this mechanism is thought to be singlet oxygen,



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which is more reactive than triplet oxygen and enhances bleaching and oxidation power. [See Jörg Hoffmann, Gerard Just, Wilhelm Pritzkow, Harald Schmidt, Journal Praktische Chemie/Chemiker-Zeitung, Vol. 334, Iss. 4, pp 293-297 (1992)].

**[0080]** The above self-reaction decomposition process may be inhibited by rapid adjustment of the solution pH from alkaline (pH>10.5) to acidic (pH <7), and the yield of peracetic acid is increased by increasing the rate of pH adjustment.

**[0081]** As disclosed herein, the above self-reaction decomposition process at alkaline pH ($7.5 \leq pH \leq 10.5$) may also be inhibited by addition of an appropriate peroxide stabilizer without adjusting the pH out of this range.

**[0082]** The invention may be further understood by the following non-limiting examples. All references cited herein are hereby incorporated by reference to the extent not inconsistent with the disclosure herewith. Although the description herein contains many specificities, these should not be construed as limiting the scope of the invention, but as merely providing illustrations of some of the presently preferred embodiments of the invention. For example, the scope of the invention should be determined by the appended claims and their equivalents, rather than by the examples given.

**[0083]** Flow-charts of exemplary processes of the invention for production of POA (and PAA) are provided in **FIGS. 1-2**. In **FIG. 1**, electrolytically produced caustic $H_2O_2$ is removed from the cathode chamber of electrolysis device and mixed with an acyl or acetyl donor to generate POA solutions. POA composition from the mixing chamber is introduced into a reactor chamber, thereby providing further processing capability. For example, the POA product removed from the reactor can have a precisely user-controlled pH level. The introduction location will depend on the particular reactor, and could range from a central chamber (in a three-chamber system) to an anode chamber (in a two-chamber system), as described herein. Alternatively, **FIG. 2** illustrates an embodiment where the POA composition is used "directly."

EXAMPLE 1: Non-Equilibrium PAA production Using a Three-Chamber Reactor

**[0084]** **FIG. 3** schematically illustrates a process of the invention for generating peracetic acid and other peroxyacids using an electrolytic reactor that generates hydrogen peroxide and caustic (base) from electricity, water, oxygen, electrolyte salts and acetyl donors or peroxyacid donors.

**[0085]** The electrolytic reactor in this example is composed of three flow chambers, one containing an anode (anode chamber), one containing a cathode (cathode chamber) and one disposed in between (central chamber) that does not contain an electrode. The three chambers are separated by cation exchange



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membranes where the one adjacent to the anode chamber is designated as the anode membrane and the one adjacent to the cathode is the cathode membrane. The anode and cathode electrodes are connected to a power supply (not shown). External to the electrolytic reactor is a mixing device where the caustic hydrogen peroxide solution produced at the cathode is mixed with the acetyl donor containing solution to generate PAA.

**[0086]** The general operating principal of electrolytic reactor is summarized in the following equations (4)-(6). The mixing chamber in the illustrated embodiments is optionally incorporated within the reactor, so long as the chamber interior volume is electrically "isolated" from the cathode and anode chambers. The two electron reduction of oxygen in the presence of water at a cathode surface that supplies electrons to the reaction produces hydroxide and hydrogen peroxide anions. Balancing the electrons consumed and ionic charge generated at the cathode is oxidation of water at the anode, which releases two molar equivalents of electrons and generates ½ molar equivalent of oxygen ($O_2$) and two molar equivalents of protons. To complete the electrolytic process, the protons migrate under the influence of the applied electric field gradient from the anode chamber to the cathode chamber through the cation exchange membranes and solution contained in the central chamber. The protons, upon arrival to the cathode chamber, ion pair with the hydroxide and hydrogen peroxide anions forming water and hydrogen peroxide.

(4) cathode reaction: $O_2 + H_2O + 2e^- \longrightarrow HOO^- + HO^-$

(5) anode reaction: $H_2O \longrightarrow 2H^+ + 1/2\ O_2 + 2e^-$

(6) ion pairing: $2H^+$ (from anode reaction) + $HOO^-$ + $HO^- \longrightarrow$ HOOH + HOH (in catholyte)

**[0087]** If, on the other hand, the protons migrating from the anode are partially or completely captured and replaced with alkali metal cations (e.g., sodium and/or potassium ions) then the alkali metal cations will instead migrate to the cathode chamber under the influence of the electric field gradient. The alkali metal cations will then ion pair with the hydroxide and hydrogen peroxide anions forming caustic (sodium or potassium hydroxide) and sodium hydrogen peroxide or potassium hydrogen peroxide in the equations (7)-(9) below.

(7) cathode reaction: $O_2 + H_2O + 2e^- \longrightarrow HOO^- + HO^-$

(8) anode reaction: $H_2O \longrightarrow 2H^+ + 1/2\ O_2 + 2e^-$



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(9) ion pairing (in catholyte): $2Na^+$ (from anolyte electrolyte or central chamber electrolyte)+ $HOO^- + HO^- \longrightarrow$ HOONa + HONa

**[0088]** The source of alkali metal cations can be in the form of a salt (sulfate, phosphate, acetate, citrate, bicarbonate, bisulfate etc.) or base (NaOH, KOH, NaOOH, KOOH, etc.) or caustic hydrogen peroxide product from the reactor or caustic peracetic acid product. In a preferred embodiment, the source of alkali metal cations is the caustic peracetic acid product. The alkali metal cation source may comprise in whole or in part the anode solution or central chamber solution. The protons generated at the anode are captured by ion pairing with the above listed anions whereby some or all of the alkali metal cations are liberated and become mobile charge carriers (ionized and mobile in solution and through a membrane) that migrate under the influence of the electric field gradient to the cathode.

**[0089]** In an aspect, any of the systems and methods described herein are further characterized in terms of a molar ratio (also referred herein as a "concentration ratio") of ions in the anolyte solution, and more specifically of the anolyte solution in the anode chamber. In an aspect, the molar ratio of alkali metal ions (e.g., $Na^+$ or $K^+$) to protons (e.g., $H^+$) in the anode chamber is greater than 1, greater than 3, or is greater than 10. As discussed, there are many different means for generating alkali metal ions. An important feature provided herein is preferentially increasing alkali metal ions in the anode chamber to provide a buffer so that amount of available protons is minimized.

**[0090]** In an embodiment for $Na^+/H^+$ Molar ratio (or $K^+/H^+$ Molar ratio) in the anolyte solution for a two chamber reactor configuration and Nafion® as the membrane: The $Na^+/H^+$ ratio should be greater than 1 to have useful alkaline hydrogen peroxide production Faradaic efficiency; preferably the $Na^+/H^+$ ratio is greater than 3 for greater alkaline hydrogen peroxide production efficiency; and ideally this ratio is greater than 10 for the highest alkaline hydrogen peroxide production efficiencies. (There are no efficiency limitations created by the ratio being in greater excess.) The higher the $Na^+/H^+$ ratio, the greater proportion of sodium transport through the membrane over protons to support the production of alkaline hydrogen peroxide.

**[0091]** If so desired, one may reduce this ratio to ca. 3-4 to allow some amount of acid protons to be transported through the membrane from the anolyte to the catholyte. This may be advantageous in some cases to reduce the concentration of hydroxide in the catholyte, thereby increasing the efficiency of the conversion yield of the acetyl donor to the peroxycarboxylic acid when the acetyl donor is mixed with the alkaline



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hydrogen peroxide solution. The reaction of excess hydroxide with an acetyl donor simply produces the carboxylic acid.

**[0092]** It is understood that these ratios refer to steady-state systems and that there may be a start-up period of time, such as during continuous mode operation where there is a periodic recycling of a reagent such as peroxycarboxylic acid, where steady state has not been achieved and that the ratio is less than 1. In an aspect, the ratios provided herein intend to refer to the ratio achieved during steady state conditions after the start-up period.

**[0093]** By the above mechanism the cations supplied, for example, to the central chamber solution (or alternatively to the anode chamber solution) are transported to the cathode solution under the influence of the electric field gradient. This process is herein referred to as "electrodialysis". By the above mechanism, the alkali metal cations present in a process' cathode solution can be recycled back into an unprocessed cathode solution by passing the processed cathode solution through the central chamber. By the above mechanism, the alkali metal cations present in a processed cathode solution mixed with an acetyl donor to produce peracetic acid may be recycled back into the unprocessed cathode solution by passing the processed cathode solution mixed with an acetyl donor through the central chamber. By the above mechanism, the alkali metal cations present in a cathode solution mixed with a peroxyacid donor to produce a peroxyacid can be recycled back into the cathode solution by passing the cathode solution through the central chamber. A process utilizing one or more of these recycling steps is referred to herein as a "continuous process." A continuous process need not run continuously, but instead refers to this recycling and can be interrupted as needed and supplemented with one or more substituents such as a top-up of water or one or more other reagents. Accordingly, any of the processes or systems described is performed in continuous mode.

**[0094]** When there is more than one type of mobile charge carrier in the system the relative concentrations of each charge carrier type reaching the cathode can be controlled. For example, adjusting the concentration of alkali metal source in the central chamber solution and/or adjusting the type of anion in the central chamber solution will adjust the ratio and/or mobility of protons versus alkali metal cations reaching the cathode chamber. This in turn adjusts the ratio of ion pairing between protons, alkali metal cations, hydroxide, and peroxide anions.

**[0095]** Protons will preferentially ion pair with the stronger base, hydroxide in this case, to form water thereby reducing the hydroxide concentration more rapidly than the



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peroxide anion concentration (hydrogen peroxide is a weak acid with a $pK_a$ of 11.6). Reducing the hydroxide to peroxide ratio is desirable to maximize the chemical conversion of the acetate or peroxyacid donor to the desired peracetic acid or peroxyacid product instead of the corresponding carboxylic acid. As noted, the hydroxide competes for reaction with the acetyl donor to produce acetic acid.

**[0096]** The process illustrated in **FIG. 3** is summarized by the flow-charts of **FIG. 1**. **FIG. 1** reflects an embodiment where: (1) A caustic hydrogen peroxide product is electrolytically produced at the cathode. (2) The caustic hydrogen peroxide product is removed from the reactor and (3) mixed with a source of acetyl donors or peroxyacid donors (single or mixture) and optionally salts and/or peroxide stabilizers to form a solution containing peracetic acid or other peroxyacids. (4) The peracetic acid or peroxyacid containing solution formed in step (3) is then passed back through a different flow chamber in the electrolytic reactor disposed between the anode and cathode flow chambers, partitioned from the cathode and anode flow chambers by ion exchange membranes. During passage of the peracetic acid or peroxyacid containing solution through the central flow chamber of the reactor alkali metal cations are transported by electrodialysis through the cathode membrane and recycled back into the caustic hydrogen peroxide solution production process at the cathode. Alkali metal cations are removed from the peracetic acid or peroxyacid containing solution and are replaced by acid protons produced by electrolytic oxidation of water at the anode and transported through the anode membrane by the applied electric field gradient. This ion transport and electrodialysis process lowers the pH of the peracetic acid or peroxyacid containing solution to a suitable pH range, preferably pH 7 or lower, where peracetic acid and peroxyacids are most stable.

**[0097]** **FIG. 2** summarizes another embodiment, where step (4) involving the peracetic acid or peroxyacid containing solution formed in step (3) being used directly for an application requiring elevated pH, such as a pH greater than 11 in some embodiments (example of such an application is pulp bleaching). A salt electrolyte containing alkali metal cations is added to the anolyte or central chamber solutions to provide the cations required by the above process to produce caustic peroxide at the cathode.

**[0098]** There are several useful features related to this example, including: (1) preventing the acetyl donor from contacting an electrode of the reactor where the acetyl donor may be electrolytically degraded or deactivated or the acetyl donor may foul the electrode surface; (1a) preventing the acyl donor from contacting an electrode of the



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reactor where the acetyl donor may be electrolytically degraded or deactivated or the acyl donor may foul the electrode surface; (2) producing peracetic acid or peroxycarboxylic acids from electrolytically generated hydrogen peroxide and hydrogen peroxide ions from stable precursors, non-toxic precursors, and non-hazardous precursors on-site and on-demand; (3) producing peracetic acid or peroxycarboxylic acids from electrolytically generated hydrogen peroxide and hydrogen peroxide ions in the absence of an electrode so that all peroxide species are preserved in the product stream; (4) producing peracetic acid or peroxycarboxylic acids from electrolytically generated hydrogen peroxide and hydrogen peroxide ions in the absence of a cathode so that all peracetic acid and peroxycarboxylic acids are preserved in the product stream; (5) producing peracetic acid or peroxycarboxylic acids from electrolytically generated hydrogen peroxide and hydrogen peroxide ions in the presence of an anode so that hydrogen peroxide concentration may be decreased in the product stream; (6) producing alkaline electrolyte from a salt rather than adding alkaline chemical feedstocks; (7) controlling the catholyte pH and peroxide to hydroxide ratio by balancing the transfer rates of alkali metal cations and acid protons through the cathode membrane into the catholyte where the cation transfer is driven primarily by electrodialysis; (8) adjusting the pH of the peracetic acid products using electrodialysis to replace alkali metal cations with acid protons generated at the anode; (9) recovering alkali metal cations from the peracetic acid or peroxyacid products using electrodialysis to transfer cations to the catholyte where they are recycled back into the process for producing caustic (alkaline) hydrogen peroxide. An advantage of keeping the acetyl donor and peracetic acid product out of contact with an electrode include avoiding electrolysis of the acetyl donor or PAA product or $H_2O_2$ to inactive forms. Advantages of passing the alkaline PAA product solution through the reactor (central or anode chambers) include automated pH adjustment without the use of bulk chemicals and recovery of alkali metal ions back into the process (minimizes consumables). Advantages of passing the alkaline PAA product through the anode chamber include automated pH adjustment without the use of bulk chemicals; recovery of alkali metal ions back into the process (thereby minimizing the amount of consumables introduced to the reactor); reduction of the $H_2O_2$ concentration (thereby minimizing corrosivity of PAA product); and reduction of the acetyl donor byproduct concentration (thereby reducing organic content).

**[0099]** Additionally, the materials in the reactor system that are contacted by peracetic acid or peroxyacids are preferably compatible and do not cause significant



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degradation of the peroxyacid products (this includes reactive or catalytic materials, leachable materials, material degradation byproducts, etc.). The materials of the reactor system that are contacted by caustic peracetic acid or peroxyacids products should be compatible and not cause significant degradation of the caustic peroxyacid products (this includes reactive or catalytic materials, leachable materials, material degradation byproducts, etc.). These materials include fluid lines, mixing devices, wetted pump parts, gaskets, membranes, wetted reactor body parts, flow frames, other objects contained within the reactor (screens, fibers, ion exchange resins, particles, etc.) fluid reservoirs, storage tanks, valves, fittings, meters, sensors, etc.

**[00100]** Preferred metals and metal alloys compatible as wetted parts in the reactor system include stainless steel (austenitic alloys), titanium, zirconium, Inconel alloys, Hastelloy alloys. Preferred plastics, elastomers, rubbers and polymers compatible as wetted parts in the reactor system include polypropylene, polysulfone, polyvinylchloride (PVC), chlorinated polyvinylchloride (CPVC), Teflon(R), polytetrafluoroethylene (PTFE), polyvinyldifluoride (PVDF, Kynar), Kel-F, polymethyl methacrylate resins (acrylics), acrylonitrile butadiene styrene (ABS) resins, ethylene propylene diene M-class (EPDM), Viton fluoroelastomers (composed of at least two of the following: hexafluoroethylene, vinylidene fluoride, tetrafluoroethylene, and perfluoromethylvinlyethers).

**[00101]** Preferred cathode materials include carbon-based materials such as graphite, carbon fiber, carbon felt, graphite felt, carbon black, activated carbon, carbon aerogels, and carbon nanotubes having native surfaces or surfaces modified with carbon oxides, catalytic organic molecules, catalytic metals and/or metal oxides, halogenated surfaces, thermoplastics (e.g., PTFE), electropolymers (e.g., polypyrrole, polypyridine) and combinations thereof appropriate for the electrochemical reduction of oxygen to peroxide, peroxide ions, and peroxide radicals. In an embodiment preferred cathode materials include metal-based materials such as nickel, stainless steel alloys, Inconel alloys coated with graphite, graphene, carbon black, activated carbon, carbon aerogels, carbon nanotubes, thermoplastics, carbonized thermoplastics, gold, palladium, platinum, iridium and alloys and their respective oxide forms; or specific metal oxides such as oxides of the lanthanides and mixtures of two or more of the metal oxides such as cerium oxide, copper oxide, manganese oxide, iron oxide, silver oxide, nickel oxide, palladium oxide, platinum oxide, iridium oxide.

**[00102]** Preferred anode materials include titanium, anodized titanium supported metal oxides such as iridium oxide, doped iridium oxides, lanthanum oxides and



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platinized titanium. In a preferred embodiment, the anode is a dimensionally stable anode (DSA) comprising a titanium supported electrocatalyst.

**[00103]** Preferred membrane materials include ion exchange resin membranes and microporous membrane products composed of preferred plastics and polymer resins compatible with the process solutions. In a preferred embodiment the membrane is a Nafion(R) ion exchange membrane.

**[00104]** Wetted parts of the reactor system are treated prior to generation of peroxide species. All wetted surfaces are washed with a degreasing fluid such as Blue Gold(TM) or alcohol (e.g., methanol, ethanol, isopropanol) to remove organic materials and soils followed by rinsing with demineralized water. Wetted stainless steel parts are passivated with citric acid or nitric acid at concentrations of at least 5 wt% in warm water heated to at least 35 degrees Centigrade followed by rinsing with demineralized water. Membranes are pre-treated by soaking in alkaline hydrogen peroxide overnight. Any wetted surfaces in contact with peroxycarboxylic acids may also be pre-soaked in alkaline peracetic acid to remove or extract any reactive materials that can react with and consume peroxycarboxylic acid products. Electrodes are prepared according to procedures specific for each particular electrode type and material.

**[00105]** The mixing device for the acetyl donors indicated schematically in Figure 3 (as well as in Figures 4-6) to mix the acetyl or acyl donor materials with the alkaline hydrogen peroxide solution to promote their reaction to produce peroxycarboxylic acids. Several approaches and apparatus may be used to carry out the mixing. Approaches include active mixing, passive mixing, induction, and injection methods. Apparatus effective in this invention include mechanically stirred tanks, centrifugal mixers, centrifugal pumps, static mixers, eductors, venturi mixers, and injector tubes and nozzles. The acetyl or acyl donor may be introduced to such apparatus by means of dosing pumps, metering pumps, peristaltic pumps, gravity feed, solenoid valve feed, rotary valve feed, and pressure driven feed mechanisms utilizing pneumatic or hydraulic driving forces. The mixture of alkaline hydrogen peroxide and acetyl or acyl donor is provided a reaction time (also called residence time or dwell time or cure time) in the mixing apparatus that allows the formation of the peroxyacetic acid product to occur. The reaction time is preferably adjusted to maximize peroxycarboxylic acid yield prior to pH adjustment, stabilization or use. After the selected reaction time, the peroxyacetic acid product is circulated or passed through the central reactor chamber in Figure 3, (or circulated or passed through the central reactor chamber in Figures 4 and 5, or not passed through the reactor in Figure 6)



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**[00106]** An advantage of the acetyl or acyl donor dosing and mixing approach is the ability to use materials in the form of a solid, liquid, dispersion, suspension or combination of such forms. The acetyl or acyl donor may also have limited or minimal solubility in alkaline hydrogen peroxide solution and be mixed as a two-phase system until reaction has occurred. Alternatively, an organic cosolvent may be dosed into the mixture to increase solubility.

**[00107]** In a preferred embodiment an acetyl or acyl donor in liquid form is injected into an alkaline hydrogen peroxide solution flowing through a venturi mixer followed by a cure time set by the residence time spent traveling through a transfer line of an appropriate length, Figure 7. The resulting peroxycarboxylic acid solution is transferred to the anode of the reactor to adjust the product pH, recover electrolyte, and lower the residual hydrogen peroxide concentration.

**[00108]** In an embodiment the acetyl or acyl donor is sparingly soluble in alkaline hydrogen peroxide solution resulting in a two phase mixture or dispersion of immiscible liquids. In an embodiment the acetyl or acyl donor dissolution rate is slow in alkaline hydrogen peroxide solution resulting in a two phase mixture, dispersion or suspension.

**[00109]** In an embodiment the peroxycarboxylic acid product is soluble in alkaline hydrogen peroxide solution. In an embodiment the peroxycarboxylic acid product is soluble in acidic solution. In an embodiment the peroxycarboxylic acid product is soluble in water. In an embodiment the peroxycarboxylic acid product is not soluble in the alkaline or acidified product fluid and is recovered as a separate phase by an appropriate means such as precipitation, centrifugation, hydrocyclone separation or filtration.

**[00110]** In an embodiment the acetyl or acyl donor byproduct is soluble in alkaline hydrogen peroxide solution. In an embodiment the acetyl or acyl donor byproduct is soluble in acidic solution. In an embodiment the acetyl or acyl donor byproduct is soluble in water. In an embodiment the acetyl or acyl donor byproduct is sparingly soluble in alkaline hydrogen peroxide solution resulting in a two phase mixture or dispersion of immiscible liquids. In an embodiment the acetyl or acyl donor byproduct is not soluble in the alkaline or acidified product fluid and is recovered as a separate phase by an appropriate means such as precipitation, centrifugation, hydrocyclone separation or filtration.

**[00111]** Figure 7 indicates three possible locations for makeup electrolyte to enter the generator system. "Makeup Electrolyte Location 1" represents addition of electrolyte into the catholyte solution reservoir either directly or carried in the makeup water.



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"Makeup Electrolyte Location 2" represents addition of electrolyte into the anolyte solution reservoir or anode circulation loop through the reactor. "Makeup Electrolyte Location 3" represents addition of electrolyte into the mixing stage where the catholyte solution and acetyl or acyl donor materials are mixed. Alternatively, the makeup electrolyte may be combined with the acetyl or acyl donor as a single input into the mixing stage.

**[00112]** The makeup electrolyte may be in the form of a solid, liquid, solution or suspension. Preferred methods of adding solid makeup electrolyte to the generator system include solid chemical feeders such as augers or rotary valve mechanisms. Preferred mechanisms of adding liquid makeup electrolyte (solution, liquid suspension) include chemical feeders such as dosing pumps, peristaltic pumps, gravity, pressure and vacuum.

EXAMPLE 2: Batch mode operation

**[00113]** A cathode starting solution consisting of 1.42 g sodium sulfate in 2.0 L of deionized water is added to the catholyte reservoir. An anode solution consisting of 5.56 mL concentrated sulfuric acid in 1.0 L of deionized water is added to the anolyte reservoir. A central chamber solution consisting of 14.2 g sodium sulfate in 1.0 L of deionized water is added to the central chamber reservoir. All three solutions are circulated through their respective flow chambers, as summarized in **FIG. 3**.

**[00114]** The circulating catholyte solution is oxygenated while a current density of 300 $A/m^2$ is applied to the electrodes for 3 hours using a digital DC power supply operated in current control mode. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution giving a cathode product containing 2.04 g/L $H_2O_2$ at pH 11.4 at which time the reactor is turned off. The sodium ion concentration measured in the central chamber solution is depleted from the starting concentration of 4.39 g/L to a final concentration of 1.83 g/L. The catholyte product solution and central chamber solution are drained from the reactor.

**[00115]** 2.0 L of catholyte product is mixed in a separate container with 11.69 g of acetylsalicylic acid and 10.65 g sodium acetate trihydrate and this mixture is stirred for 15 minutes. This final mixture is added to the central chamber reservoir. A new catholyte starting solution of 1.42 g sodium sulfate in 2.0 L of deionized is added to the catholyte reservoir.

**[00116]** The reactor is restarted and all three solutions (anolyte, catholyte and central chamber) are circulated through their respective flow chambers. The circulating catholyte solution is oxygenated while a current density of 300 $A/m^2$ is applied to the



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electrodes for 1 hour. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution. The central chamber solution (or peracetic acid product solution) contains 1.3 g/L peracetic acid, and salicylic acid and acetate byproducts at a pH of 4.4. The sodium ion concentration measured in the central chamber solution is depleted from the starting concentration of 2.53 g/L to a final concentration of 1.67 g/L.

**[00117]** In another batch operation example, a cathode starting solution of 1.42 g sodium sulfate in 2.0 L of deionized water is added to the catholyte reservoir. An anode solution of 5.56 mL concentrated sulfuric acid in 1.0 L of deionized water is added to the anolyte reservoir. A central chamber solution of 51.7 g sodium acetate trihydrate in 2.0 L of deionized water is added to the central chamber reservoir. All three solutions are circulated through their respective flow chambers as provided in **FIG. 3**.

**[00118]** The circulating catholyte solution is oxygenated while a current density of 300 $A/m^2$ was applied to the electrodes for 4 hours using a digital DC power supply operated in current control mode. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution giving a cathode product containing 2.86 g/L $H_2O_2$ at pH 12.3 at which time the reactor is turned off. The sodium ion concentration measured in the central chamber solution is depleted from the starting concentration of 4.15 g/L to a final concentration of 1.22 g/L. The catholyte product solution and central chamber solution are drained from the reactor.

**[00119]** 2.0 L of catholyte product is mixed in a separate container with 27.50 g of acetylsalicylic acid and 14.40 g sodium acetate trihydrate and this mixture is stirred for 15 minutes. This final mixture is added to the central chamber reservoir. A new catholyte starting solution of 1.42 g sodium sulfate in 2.0 L of deionized is added to the catholyte reservoir.

**[00120]** The reactor is restarted and all three solutions (anolyte, catholyte and central chamber) are circulated through their respective flow chambers. The circulating catholyte solution is oxygenated while a current density of 300 $A/m^2$ is applied to the electrodes for 1 hour. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution. The central chamber solution (or peracetic acid product solution) contains 2.7 g/L peracetic acid, less than 0.4 g/L hydrogen peroxide, and salicylic acid and acetate byproducts at a pH of 5.4. The sodium ion concentration measured in the central chamber solution is depleted from the starting concentration of 4.89 g/L to a final concentration of 4.00 g/L.

**[00121]** Continuous mode. In other embodiments the batch production process is modified to work as a continuous production process by drawing off a constant stream



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of catholyte product directly from the catholyte circulation loop, passing the catholyte product through a mixer (mixing chamber) that is dosed with the acetyl donor, and then passing the mixture through the central chamber with the proper residence time in a single pass. A makeup water stream to the catholyte solution replenishes the catholyte product draw-down volume in the process. This process is illustrated in **FIG. 3**

**[00122]** **FIGs. 4-6** illustrate various two-chamber embodiments, and are further discussed as Examples 3-5.

EXAMPLE 3: Two-chamber, pH shift of PAA composition

**[00123]** **FIG. 4** is a two-chamber configuration, wherein the caustic PAA composition is passed over the anode as anolyte solution to shift the pH from caustic to acid. Sodium and/or potassium cations are recovered back into the cathode process.

EXAMPLE 4: Two-chamber, rapid pH shift by acidic anolyte loop

**[00124]** **FIG. 5** is a two-chamber configuration, wherein the caustic PAA product is dosed into an acidic anolyte loop to very rapidly shift the pH from caustic to acid. Cations (such as sodium and/or potassium, for example) are recovered back into the cathode process.

EXAMPLE 5: Two-chamber, direct use of caustic PAA composition

**[00125]** **FIG. 6** is a two-chamber configuration, wherein the caustic PAA product is used directly. Sodium and/or potassium cations are not recovered back into the cathode process. Sodium or potassium feedstock is added in the form of sodium or potassium hydroxide in the 'base containing source.'

**[00126]** Alternatively, the sodium or potassium feedstock is added as a salt or hydroxide into the anode loop to produce caustic hydrogen peroxide, as in the previous example, to be mixed with the acetyl donor.

**[00127]** The caustic PAA is particularly useful for bleaching in applications such as pulp and paper and textiles.

EXAMPLE 6: Batch operation, 2-chamber reactor using triacetin donor

**[00128]** A cathode starting solution of 1.42 g sodium sulfate in 2.0 L of deionized water is added to the catholyte reservoir. An anode solution of 10.62 mL of 30% peracetic acid and 0.71 g sodium sulfate in 1.0 L of deionized water is adjusted to pH



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11.2 with sodium hydroxide and added to the anolyte reservoir. Catholyte and anolyte solutions are circulated through their respective flow chambers.

**[00129]** The circulating catholyte solution is oxygenated while a current density of 300 A/m$^2$ is applied to the electrodes for 4 hours using a digital DC power supply operated in current control mode. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution giving a cathode product containing 3.32 g/L $H_2O_2$ at pH 11.6 at which time the reactor is turned off. The sodium ion concentration measured in the anolyte solution is depleted from the starting concentration of 3.06 g/L to a final concentration of 0.130 g/L. The anolyte solution is drained from the reactor.

**[00130]** 1.0 L of catholyte product is transferred to the empty anolyte reservoir. To this solution is added 3.05 mL of triacetin and this mixture is stirred for 15 minutes. This mixture contained 2.09 g/L peracetic acid and 2.13 g/L hydrogen peroxide and approximately 1.46 g/L sodium ion concentration. 1.0 L of deionized water is added to the remaining catholyte solution in the catholyte reservoir.

**[00131]** The reactor is restarted and the catholyte and anolyte solutions are circulated through their respective flow chambers. The circulating catholyte solution is oxygenated while a current density of 300 A/m$^2$ is applied to the electrodes for 1.5 hours. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution. The anolyte solution (or peracetic acid product solution) contains 1.14 g/L peracetic acid and 0.26 g/L hydrogen peroxide at a pH of 3.6. The sodium ion concentration measured in the anolyte product solution is 0.409 g/L.

EXAMPLE 7: Dependence of PAA decomposition during pH, temperature adjustment (3-Chamber Reactor).

**[00132]** For all three exemplary data sets below, PAA solutions are prepared by dissolving the appropriate volume of $H_2O_2$ (30%), along with 3.55 g of anhydrous sodium sulfate (0.05M) in 500 mL of deionized water. The pH is adjusted to 11.4 with sodium hydroxide pellets. Triacetin is then added via volumetric pipette. The solution is stirred for 15 minutes and the PAA concentration determined by titration with sodium thiosulfate to give the initial yields shown in Table 1. The pH of the solution is then adjusted by circulation through the central chamber of the electrolytic cell run at 3.0A. Once the pH turns acidic, a final yield of PAA is determined by titration.

**[00133]** Dependence of PAA decomposition on temperature during pH adjustment (2-Chamber – PAA solutions prepared as above) is summarized in TABLE 2.



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**[00134]** High concentration solution of caustic PAA can be diluted before pH adjustment to minimize loss (PAA solutions prepared as above) is summarized in TABLE 3.

**[00135]** Without being bound by any particular theory, there are proposed reasons for loss of PAA yield during pH adjustment. PAA losses during pH adjustment are due to (1) auto-decomposition of the peracetic acid species, which is accelerated at high pH and (2) decomposition by a self reaction between peracetic acid anion and peracetic acid, which is accelerated near the pKa of peracetic acid of 8.2 [Jörg Hoffmann, Gerard Just, Wilhelm Pritzkow, Harald Schmidt, Journal für Praktische Chemie/Chemiker-Zeitung, Vol. 334, Iss. 4, pp 293-297 (1992)]. PAA in the pH range between approximately 7.5 and 10.5 is particularly sensitive to decomposition unless there is a suitable stabilizer present such as salicylic acid or acetylsalicylic acid, phosphonic acid derivatives, Dequest®, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), or others. Accordingly, in some embodiments the pH of the cathode products is above about 10.5, thereby minimizing this decomposition affect.

**[00136]** The use of a peroxide stabilizer such as Dequest® provides a stabilizing effect to PAA in the pH range where decomposition is accelerated as summarized in Table 4.

**[00137]** Caustic peroxide solutions are prepared at pH 11.4. Triacetin and Dequest® are added and the solutions stirred for fifteen (15) minutes. The pH is then adjusted with glacial acetic acid and the solutions stirred for an additional sixty (60) minutes.

EXAMPLE 8: pH adjustment in anode chamber of reactor with the use of Dequest® stabilizer.

**[00138]** An aqueous solution is made containing 6.68 mL $H_2O_2$ (30%) and 7.1 g sodium sulfate dissolved in 1 L total volume of deionized $H_2O$. The pH is adjusted to 11.41 with NaOH pellets. 4.0 mL of triacetin is added to this solution along with 0.29 g of Dequest®. The solution is stirred for 10 minutes and the resulting solution contains 2090 ppm PAA at pH 10.6. 500 mL of this PAA solution is circulated through the anode chamber while a cathode starting solution of 1.42 g sodium sulfate in 2.0 L of deionized water is circulated through the cathode chamber. The circulating catholyte solution is oxygenated while a current density of 300 $A/m^2$ is applied to the electrodes. After 30 minutes of electrolysis the anolyte solution contains 1900 ppm PAA at a pH of 4.5. The PAA concentration decreases by 9% during the pH adjustment in the reactor. This loss



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is in contrast to what is typically near a 30% loss without the use of a stabilizer at comparable PAA concentration as summarized in Tables 1 and Table 3.

Example 9- Continuous operation, 2-chamber reactor using triacetin donor

**[00139]** The continuous production system has two stages of operation. The first stage is the startup stage during which the internal process fluids are brought up to steady state operating conditions including pH, electrolyte strength, solution volume, hydrogen peroxide concentration, sodium hydroxide concentration, and peracetic acid concentration. The second stage is the continuous production stage during which peracetic acid product solution is generated at a constant rate, pH and composition.

**[00140]** For the startup stage of system operation, a cathode starting solution of 7.22 g sodium sulfate in 7.0 L of deionized water is added to the catholyte reservoir **(Figure 5)**. An anode starting solution of 58.5 g sodium sulfate and 67.5 g sodium acetate in 2.0 L of deionized water is added to the anolyte reservoir. Catholyte and anolyte solutions are circulated through their respective flow chambers in the reactor.

**[00141]** The circulating catholyte solution is oxygenated with 1.0 L/min oxygen gas at the cathode feed pressure of ca. 18 psig while a current density of 420-480 $A/m^2$ is applied to the electrodes for using a switch mode DC power supply operated in voltage control mode. Hydrogen peroxide and caustic (NaOH) are produced in the catholyte solution, until the catholyte solution contains 6.0-7.0 g/L $H_2O_2$ at approximately pH 11.5.

**[00142]** A catholyte solution makeup water source is turned on at a rate of 20 mL/min. The makeup water source is tap water passed through an ion exchange water softening cartridge prior to entering the catholyte reservoir. Sodium sulfate is added to the catholyte solution at a rate of ca. 0.04 g/min. Simultaneously, a side-stream of the catholyte solution is drawn from the catholyte reservoir at a rate of 20 mL/min into which triacetin is dosed at a rate of 0.16 g/min. The catholyte-triacetin mixture is passed through a coil of Teflon tubing having a residence time of ca. 3 min, after which the mixture flows into the anolyte reservoir. Anolyte solution is drawn from the anolyte reservoir through an overflow tube at a rate of ca. 20 mL/min. After the peracetic acid in the anolyte solution reaches a steady state concentration of 4 g/L the startup stage of system operation is complete.

**[00143]** The continuous production stage of system operation commences by maintaining the steady-state conditions achieved with the operating conditions achieved by the completion of the startup stage. The continuous production stage of system operation produces a non-equilibrium peracetic acid solution drawn at a continuous rate



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of 20 mL/min from the anolyte reservoir having average active ingredient concentrations of 4.2 g/L peracetic acid and 0.4 g/L hydrogen peroxide.

Example 10- Continuous operation, 2-chamber reactor using triacetin donor

**[00144]** For the startup stage of system operation a cathode starting solution of 7.22 g sodium sulfate in 7.0 L of deionized water is added to the catholyte reservoir. An anode starting solution of 1.42 g sodium sulfate and 135.5 g sodium acetate in 2.0 L of deionized water is added to the anolyte reservoir. Catholyte and anolyte solutions are circulated through their respective flow chambers in the reactor.

**[00145]** The circulating catholyte solution is oxygenated with 1.0 L/min oxygen gas at the cathode feed pressure of ca. 18 psig while a current density of 210-220 $A/m^2$ is applied to the electrodes for using a switch mode DC power supply operated in voltage control mode. Hydrogen peroxide and caustic (NaOH) are produced in the catholyte solution, until the catholyte solution contains 2.0-2.2 g/L $H_2O_2$ at approximately pH 11.5.

**[00146]** A catholyte solution makeup water source is turned on at a rate of 50 mL/min. The makeup water source is tap water passed through an ion exchange water softening cartridge prior to entering the catholyte reservoir. Sodium sulfate is added to the catholyte solution at a rate of ca. 0.04 g/min. Simultaneously, a side-stream of the catholyte solution is drawn from the catholyte reservoir at a rate of 50 mL/min into which triacetin is dosed at a rate of 0.13 g/min. The catholyte-triacetin mixture is circulated in a small reservoir having a residence time of ca. 20 min, after which the mixture passes through an overflow tube into the anolyte reservoir. Anolyte solution is drawn from the anolyte reservoir through an overflow tube at a rate of ca. 50 mL/min. After the peracetic acid in the anolyte solution reaches a steady state concentration of 0.9 g/L the startup stage of system operation is complete.

**[00147]** The continuous production stage of system operation commences by maintaining the steady-state conditions achieved with the operating conditions achieved by the completion of the startup stage. The continuous production stage of system operation produces a non-equilibrium peracetic acid solution drawn at a continuous rate of 50 mL/min from the anolyte reservoir having average active ingredient concentrations of 0.95 g/L peracetic acid and 0.15 g/L hydrogen peroxide.

**[00148]** Detailed product composition analyses was conducted on two different peracetic acid production runs in the continuous operation, 2-chamber reactor using triacetin donor similar to that described above, see Table 5. Peracetic acid and hydrogen peroxide concentrations were determined by established titration methods.



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Acetic acid and glycerol concentrations were determined by HPLC, sodium ion concentration was measured with a sodium ISE, and pH was measured with a bench top pH meter.

**[00149]** Three peracetic acid product samples collected from the anolyte reservoir of the continuous operation, 2-chamber reactor using triacetin as the acetyl donor were placed in three separate darkened HDPE bottles and stored at room temperature in darkness. At time zero and various times thereafter, the concentration of peracetic acid was measured in each of the three solution samples to determine the degradation rate in the absence of peroxide stabilizers. The average half life of the peracetic acid in the product solution was 10 days. The decay curve was approximately linear as illustrated in Fig. 8.

**[00150]** Two samples of the catholyte-triacetin mixture collected immediately upstream of the anolyte reservoir of the continuous operation, 2-chamber reactor using triacetin as the acetyl donor were placed in two separate darkened HDPE bottles and stored at room temperature in darkness. At time zero and various times thereafter, the concentration of peracetic acid was measured in each of the three solution samples to determine the degradation rate in the absence of peroxide stabilizers. The average half life of the peracetic acid in the solutions was 1.8 hours. The decay curve was approximately linear as illustrated in Fig. 9I

Example 11- Continuous operation, 2-chamber reactor using salicylic acid ethyl ester donor

**[00151]** For the startup stage of system operation a cathode starting solution of 7.22 g sodium sulfate in 7.0 L of deionized water is added to the catholyte reservoir. An anode starting solution of 120 g sodium sulfate in 2.0 L of deionized water is added to the anolyte reservoir. Catholyte and anolyte solutions are circulated through their respective flow chambers in the reactor.

**[00152]** The circulating catholyte solution is oxygenated with 1.0 L/min oxygen gas at the cathode feed pressure of ca. 18 psig while a current density of 420-480 $A/m^2$ is applied to the electrodes using a switch mode DC power supply operated in voltage control mode. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution until the catholyte solution contains 6.0-7.1 g/L $H_2O_2$ at approximately pH 11.5. The startup stage of the system is complete when the hydrogen peroxide concentration reaches the desired steady-state concentration.

**[00153]** The continuous production stage of system operation commences by supplying catholyte solution makeup water at a rate of 20 mL/min. The makeup water



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source is tap water passed through an ion exchange water softening cartridge prior to entering the catholyte reservoir. Sodium sulfate is added to the catholyte solution at a rate of ca. 0.04 g/min. Simultaneously, a side-stream of the catholyte solution is drawn from the catholyte reservoir at a rate of 20 mL/min into which salicylic acid ethyl ester is dosed at a rate of 0.95 g/min. The catholyte-salicylic acid ethyl ester mixture is passed through a coil of Teflon tubing having a residence time of ca. 3 min, after which the mixture flows into the anolyte circulation circuit outfitted with a solids separation apparatus such as a filter, centrifugal separator or settling tank. The acidified persalicylic acid precipitates from solution and is recovered from the anolyte circuit as a solid. Anolyte solution is drawn from the anolyte reservoir through an overflow tube at a rate of ca. 20 mL/min and recycled back into the catholyte makeup water or discharged.

Example 12- Continuous operation, 2-chamber reactor using n-butylmalonic acid diethyl ester donor

**[00154]** The continuous production system has two stages of operation. The first stage is the startup stage during which the internal process fluids are brought up to steady state operating conditions including pH, electrolyte strength, solution volume, hydrogen peroxide concentration, sodium hydroxide concentration, and peracetic acid concentration. The second stage is the continuous production stage during which peracetic acid product solution is generated at a constant rate, pH and composition.

**[00155]** For the startup stage of system operation a cathode starting solution of 7.22 g sodium sulfate in 7.0 L of deionized water is added to the catholyte reservoir. An anode starting solution of 120 g sodium sulfate in 2.0 L of deionized water is added to the anolyte reservoir. Catholyte and anolyte solutions are circulated through their respective flow chambers in the reactor.

**[00156]** The circulating catholyte solution is oxygenated with 1.0 L/min oxygen gas at the cathode feed pressure of ca. 18 psig while a current density of 420-480 $A/m^2$ is applied to the electrodes for using a switch mode DC power supply operated in voltage control mode. Hydrogen peroxide and caustic (NaOH) is produced in the catholyte solution until the catholyte solution contains 6.0-7.0 g/L $H_2O_2$ at approximately pH 11.5.

**[00157]** A catholyte solution makeup water source is turned on at a rate of 20 mL/min. The makeup water source is tap water passed through an ion exchange water softening cartridge prior to entering the catholyte reservoir. Sodium sulfate is added to the catholyte solution at a rate of ca. 0.04 g/min. Simultaneously, a side-stream of the catholyte solution is drawn from the catholyte reservoir at a rate of 20 mL/min into which n-butylmalonic acid diethyl ester is dosed at a rate of 0.62 g/min. The catholyte-triacetin



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mixture is passed through a coil of Teflon tubing having a residence time of ca. 3 min, after which the mixture flows into the anolyte reservoir. Anolyte solution is drawn from the anolyte reservoir through an overflow tube at a rate of ca. 20 mL/min. After the n-butyl-diperoxymalonic acid in the anolyte solution reaches a steady state concentration of approximately 14.8 g/L the startup stage of system operation is complete.

**[00158]** The continuous production stage of system operation commences by maintaining the steady-state conditions achieved with the operating conditions achieved by the completion of the startup stage. The continuous production stage of system operation produces a non-equilibrium n-butyl-diperoxymalonic acid solution drawn at a continuous rate of 20 mL/min from the anolyte reservoir having average active ingredient concentrations of 14.8 g/L the n-butyl-diperoxymalonic acid, 6.4 g/L n-butylmalonic acid, 13.1 g/L ethanol and 0.4 g/L hydrogen peroxide.

**[00159]** When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, enantiomers, and diastereomers of the group members, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. A number of specific groups of variable definitions have been described herein. It is intended that all combinations and subcombinations of the specific groups of variable definitions are individually included in this disclosure. Compounds described herein may exist in one or more isomeric forms, e.g., structural or optical isomers. When a compound is described herein such that a particular isomer, enantiomer or diastereomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer (e.g., cis/trans isomers, R/S enantiomers) of the compound described individual or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical and biological research related to the molecule or its use. Isotopic variants, including those carrying radioisotopes, may also be useful in diagnostic assays and in therapeutics. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.



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**[00160]** Molecules disclosed herein may contain one or more ionizable groups [groups from which a proton can be removed (e.g., -COOH) or added (e.g., amines) or which can be quaternized (e.g., amines)]. All possible ionic forms of such molecules and salts thereof are intended to be included individually in the disclosure herein. With regard to salts of the compounds herein, one of ordinary skill in the art can select from among a wide variety of available counterions those that are appropriate for preparation of salts of this invention for a given application. In specific applications, the selection of a given anion or cation for preparation of a salt may result in increased or decreased solubility of that salt.

**[00161]** Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

**[00162]** Whenever a range is given in the specification, for example, a temperature range, a time range, a pH range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. The upper and lower limits of the range may themselves be included in the range. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

**[00163]** All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when composition of matter are claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

**[00164]** As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. The broad term comprising is intended to encompass the narrower consisting essentially of and the even narrower consisting of. Thus, in any recitation herein of a phrase "comprising one or more claim



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element" (e.g., "comprising A and B), the phrase is intended to encompass the narrower, for example, "consisting essentially of A and B" and "consisting of A and B." Thus, the broader word "comprising" is intended to provide specific support in each use herein for either "consisting essentially of" or "consisting of." The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

**[00165]** One of ordinary skill in the art will appreciate that starting materials, catalysts, reagents, synthetic methods, purification methods, analytical methods, and assay methods, other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by examples, preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

**[00166]** All references cited herein are hereby incorporated by reference to the extent that there is no inconsistency with the disclosure of this specification. Some references provided herein are incorporated by reference to provide details concerning sources of starting materials; alternative starting materials, reagents, methods of synthesis, purification methods, and methods of analysis, reactor systems; as well as additional uses of the invention. For example, U.S. Pub 2007/0074975 (Published April 5, 2007) is hereby specifically incorporated by reference for electrochemical reactors and related methods, including systems and processes for hydrogen peroxide production. Provisional application no. 61/019,825 filed January 8, 2008 is incorporated by reference, and in particular for non-equilibrium compositions of peroxycarboxylic acid and hydrogen peroxide in water, non-equilibrium peracetic acid compositions and processes for producing these non-equilibrium mixtures.



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TABLE 1

| Triacetin (mL) | $H_2O_2$(30%) (mL) | Initial caustic PAA Yield (ppm) | PAA Yield after pH adjustment (ppm) | % loss |
|---|---|---|---|---|
| 1 | 1.67 | 760 | 684 | 10 |
| 2 | 3.34 | 1710 | 1330 | 22 |
| 2 | 5.01 | 1900 | 1330 | 30 |

TABLE 2

| Anolyte solution Temp. | Triacetin (mL) | $H_2O_2$(30%) (mL) | Initial caustic PAA Yield (ppm) | PAA Yield after pH adjustment (ppm) | % loss |
|---|---|---|---|---|---|
| >30 C | 1.25 | 4.58 | 1520 | 950 | 37 |
| ice bath cooled | 1.25 | 4.58 | 1520 | 1330 | 12 |

TABLE 3

| Triacetin (mL) | $H_2O_2$(30%) (mL) | Initial caustic PAA Yield (ppm) | Diluted caustic PAA conc. (ppm) | PAA Yield after pH adjustment (ppm) | % loss |
|---|---|---|---|---|---|
| 3.71 | 13.4 | 5890 | 589 | 475 | 19 |
| 2 | 5.01 | 1900 | not diluted | 1330 | 30 |

TABLE 4: Dequest Stabilization (500 mL) reaction mixtures#

| Triacetin (mL) | $H_2O_2$ (30%) (mL) | Dequest® (g) | Initial Caustic PAA Yield (ppm) | Adjusted pH | PAA concentration after 60 min (ppm) | % loss of PAA |
|---|---|---|---|---|---|---|
| 2.0 | 6.68 | 0 | 3116 | 9.16 | 418 | 86.6 |
| 2.0 | 6.68 | 0.044 | 3268 | 9.42 | 3230 | 1.2 |
| 2.0 | 6.68 | 0.088 | 3230 | 9.36 | 3192 | 1.2 |
| 2.0 | 6.68 | 0.176 | 3344 | 9.59 | 3230 | 3.4 |

TABLE 5

| Peracetic acid product composition from continuous 2-chamber reactor using triacetin as feedstock | | |
|---|---|---|
| Constituent | Trial 1 Concentration | Trial 2 Concentration |
| peracetic acid | 950 mg/L | 950 mg/L |
| hydrogen peroxide | 212 mg/L | 170 mg/L |
| acetic acid | 1560 mg/L | 1500 mg/L |
| glycerol | 1120 mg/L | 1110 mg/L |
| sodium | 348 mg/L | NA |
| pH | 3.40 | NA |



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We claim:

1. A method for making a peroxycarboxylic acid composition, said method comprising:

    a. electrolytically generating alkaline hydrogen peroxide or peroxide ions in a reactor comprising a cathode chamber having a cathode, an anode chamber having an anode and at least one cation exchange membrane separating said chambers;

    b. providing a source of alkali metal ions to said anode chamber such that the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than 1 and the predominant cations transported through the at least one cation exchange membrane are alkali metal ions; and

    c. reacting said hydrogen peroxide or peroxide ions with an acetyl donor to form peracetic acid in a mixing chamber that is electrically isolated from said anode and cathode of the reactor to produce the peroxycarboxylic acid composition comprising alkali metal ions.

2. The method of claim 1 wherein the source of alkali metal ions is a salt added to said anode chamber.

3. The method of claim 1 wherein the source of alkali metal ions is the peroxycarboxylic acid composition formed in step c wherein at least a portion of said composition is recycled to the anode chamber.

4. The method of any one of claims 1-3 wherein the source of alkali metal ions is added directly to the anode chamber.

5. The method of any one of claims 1-3 wherein the reactor further comprises a central chamber between the anode and cathode chambers and separated from each of said chambers by at least one cation exchange membrane and said source of alkali metal ions is added to said anode chamber, said central chamber or both.

6. The method of any one of claims 1-3 wherein the reactor further comprises a central chamber between the anode and cathode chambers and separated from



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each of said chambers by at least one cation exchange membrane and said source of alkali metal ions is added to said anode chamber, said central chamber or both and wherein the alkaline hydrogen peroxide or peroxide ions has a pH greater than or equal to 10 and less than or equal to 13.

7. The method of any one of claims 1-3 wherein the alkaline hydrogen peroxide or peroxide ions has a pH greater than or equal to 10 and less than or equal to 13.

8. The method of claim 1, wherein said reacting step further comprises

   a. introducing one or more acetyl donors to said mixing chamber; and

   b. introducing said electrolytically generated alkaline hydrogen peroxide or peroxide ions from a cathode chamber of said reactor to said mixing chamber, thereby generating said peracetic acid composition.

9. The method of any one of claims 1-3 or 8, further comprising introducing to the reactor a peroxide stabilizer, an electrolyte salt or both.

10. The method of any one of claims 1-3 wherein the peroxycarboxylic acid composition formed has a pH that is less than or equal to 8.

11. The method of any one of claims 1-3 wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than or equal to 3.

12. The method of any one of claims 1-3 wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is between about 3 and 4, inclusive.

13. The method of any one of claims 1-3 wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than or equal to 10.

14. The method of any one of claims 1-3 or 8 further comprising:

   a. introducing said peroxycarboxylic acid composition from said mixing chamber to said reactor;

   b. adjusting the pH of said peroxycarboxylic acid composition by electrodialysis; and



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c. removing said peroxycarboxylic acid composition from said reactor to obtain a peroxycarboxylic acid product solution, wherein said peroxycarboxylic acid product solution has a pH that is less than or equal 8.

15. The method of any one of claims 1-3 or 8 further comprising:

a. introducing said peroxycarboxylic acid composition from said mixing chamber to said reactor;

b. adjusting the pH of said peroxycarboxylic acid composition by electrodialysis; and

c. removing said peroxycarboxylic acid composition from said reactor to obtain a peroxycarboxylic acid product solution, wherein said peroxycarboxylic acid product solution has a pH that is less than or equal 8 and wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than or equal to 3.

16. The method of any one of claims 1-3 or 8 further comprising:

a. introducing said peroxycarboxylic acid composition from said mixing chamber to said reactor;

b. adjusting the pH of said peroxycarboxylic acid composition by electrodialysis; and

c. removing said peroxycarboxylic acid composition from said reactor to obtain a peroxycarboxylic acid product solution, wherein said peracetic acid product solution has a pH that is less than or equal 8 and wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than or equal to 10.

17. A method for making a peroxycarboxylic acid composition, said method comprising:

a. electrolytically generating hydrogen peroxide or peroxide ions in an electrochemical reactor having an anode chamber having an anode and a cathode chamber having a cathode and at least one cation exchange membrane separating the anode and cathode chambers;



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b. reacting said hydrogen peroxide or peroxide ions with an acyl or acetyl donor to form peroxycarboxylic acid, wherein said peroxycarboxylic acid is formed in a mixing chamber that is electrically isolated from said anode and said cathode;

c. introducing a salt into said rector; and

d. producing an alkaline electrolyte solution by electrodialysis of the salt introduced to said reactor, wherein said electrolyte solution adjusts the pH of said hydrogen peroxide or peroxide ions to a pH that is greater than or equal to 9.5 and less than or equal to 13.

18. The method of claim 17, further comprising adding a source of alkali metal cations to an anode chamber of said reactor.

19. The method of claim 18, wherein the ratio of concentrations of alkali metal ions to protons in said anode chamber is selected from the group consisting of: greater than or equal to 1; greater than or equal to 3, greater than or equal to 3 and less than or equal to 4; and greater than or equal to 10.

20. The method of claim 17, wherein said reactor has a catholyte solution containing said generated hydrogen peroxide or peroxide ions, said method further comprising:

a. controlling said reactor catholyte pH, wherein said catholyte pH is greater than or equal to 10 and less than or equal to 13; and/or

b. controlling a peroxide to hydroxide ratio in said catholyte solution, wherein said ratio is greater than or equal to 0.5:1 and less than or equal to 5:1.

wherein said controlling steps comprise balancing transfer rates of alkali metal cations and acid protons introduced to said catholyte solution.

21. The method of any of claims 1 and 18, wherein the ratio of concentrations of alkali metal ions to protons formed in the anode chamber is greater than 1, the alkaline hydrogen peroxide or peroxide ions has a pH greater than or equal to 10 and less than or equal to 13; and the peroxycarboxylic acid composition has a pH less than or equal to 8.



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22. The method of claim 17, wherein said peroxycarboxylic acid composition is introduced to an anode chamber of said reactor, thereby lowering said peracetic acid composition pH by electrodialysis and lowering said hydrogen peroxide concentration.

23. The method of any one of claims 1-3, 8 or 17 further comprising:

    a. introducing at least a portion of said peroxycarboxylic acid composition from said anode chamber to said mixing chamber by an acidic anolyte loop, thereby providing additional pH regulation of said peroxycarboxylic acid composition.

24. The method of any one of claims 1-3, 8 or 17 where the peroxycarboxylic acid is peracetic acid.

25., The method of any one of claims 1-3, 8 or 17 where the peroxycarboxylic acids is a substituted derivative of peroxybenzoic acid.

26. The method of any of claims 1-3, 8 and 17, wherein said peroxycarboxylic acid is a non-equilibrium composition.

27. An electrochemical reactor for generating peroxycarboxylic acid compositions, said reactor comprising:

    a. an anode positioned within an anode chamber;

    b. a cathode positioned within a cathode chamber for producing alkaline hydrogen peroxide catholyte solution;

    c. at least one cation exchange membrane separating said anode and cathode chambers;

    d. an optional central chamber between said cathode and anode chambers and separated from each of said chambers by at least one cation exchange membrane;

    e. a mixing chamber electrically isolated from said anode and cathode for receiving an acyl donor;



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f. a mixing chamber conduit for supplying said catholyte solution to said mixing chamber;

g. a peroxycarboxylic acid (POA) composition conduit for introducing POA made in said mixing chamber to said reactor, wherein said POA composition conduit is operably connected to said anode chamber or said optional central chamber; and

h. a reactor outlet for removing from said reactor at least a portion of said POA formed in said reactor.

28. The reactor of claim 27 wherein said removed POA is in a solution of lower pH than said POA made in said mixing chamber

29. The reactor of any one of claims 27 or 28, further comprising:

a. an acidic anolyte loop that operably connects said reactor outlet to said POA composition conduit, thereby providing rapid pH adjustment to said POA made in said mixing chamber.

30. The reactor of any one of claims 27 or 28, wherein said mixing chamber is positioned either external to said reactor or internal to said reactor.



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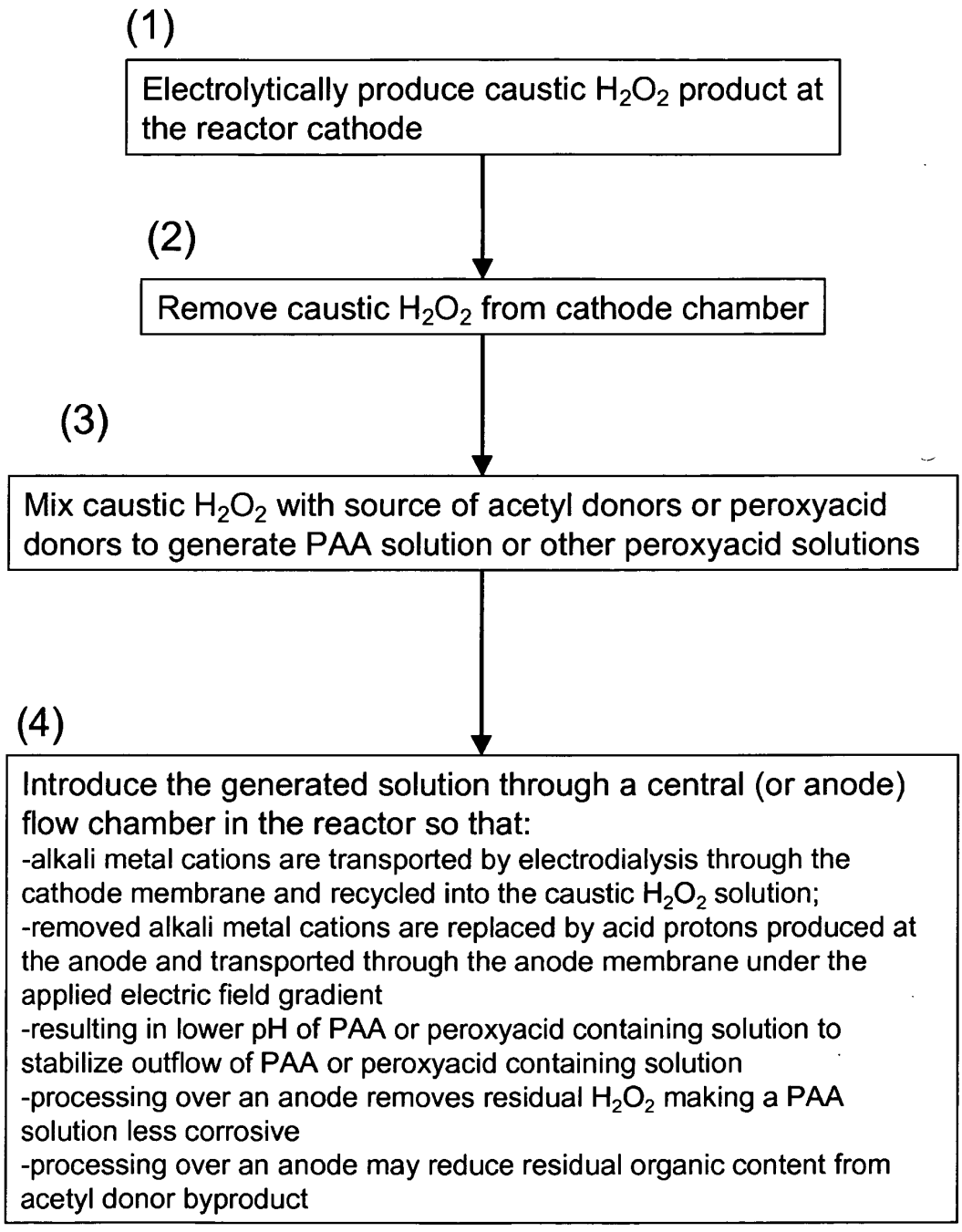

(1)
Electrolytically produce caustic $H_2O_2$ product at the reactor cathode
(2)
Remove caustic $H_2O_2$ from cathode chamber
(3)
Mix caustic $H_2O_2$ with source of acetyl donors or peroxyacid donors to generate PAA solution or other peroxyacid solutions
(4)
Introduce the generated solution through a central (or anode) flow chamber in the reactor so that:
-alkali metal cations are transported by electrodialysis through the cathode membrane and recycled into the caustic $H_2O_2$ solution;
-removed alkali metal cations are replaced by acid protons produced at the anode and transported through the anode membrane under the applied electric field gradient
-resulting in lower pH of PAA or peroxyacid containing solution to stabilize outflow of PAA or peroxyacid containing solution
-processing over an anode removes residual $H_2O_2$ making a PAA solution less corrosive
-processing over an anode may reduce residual organic content from acetyl donor byproduct

**Fig. 1**

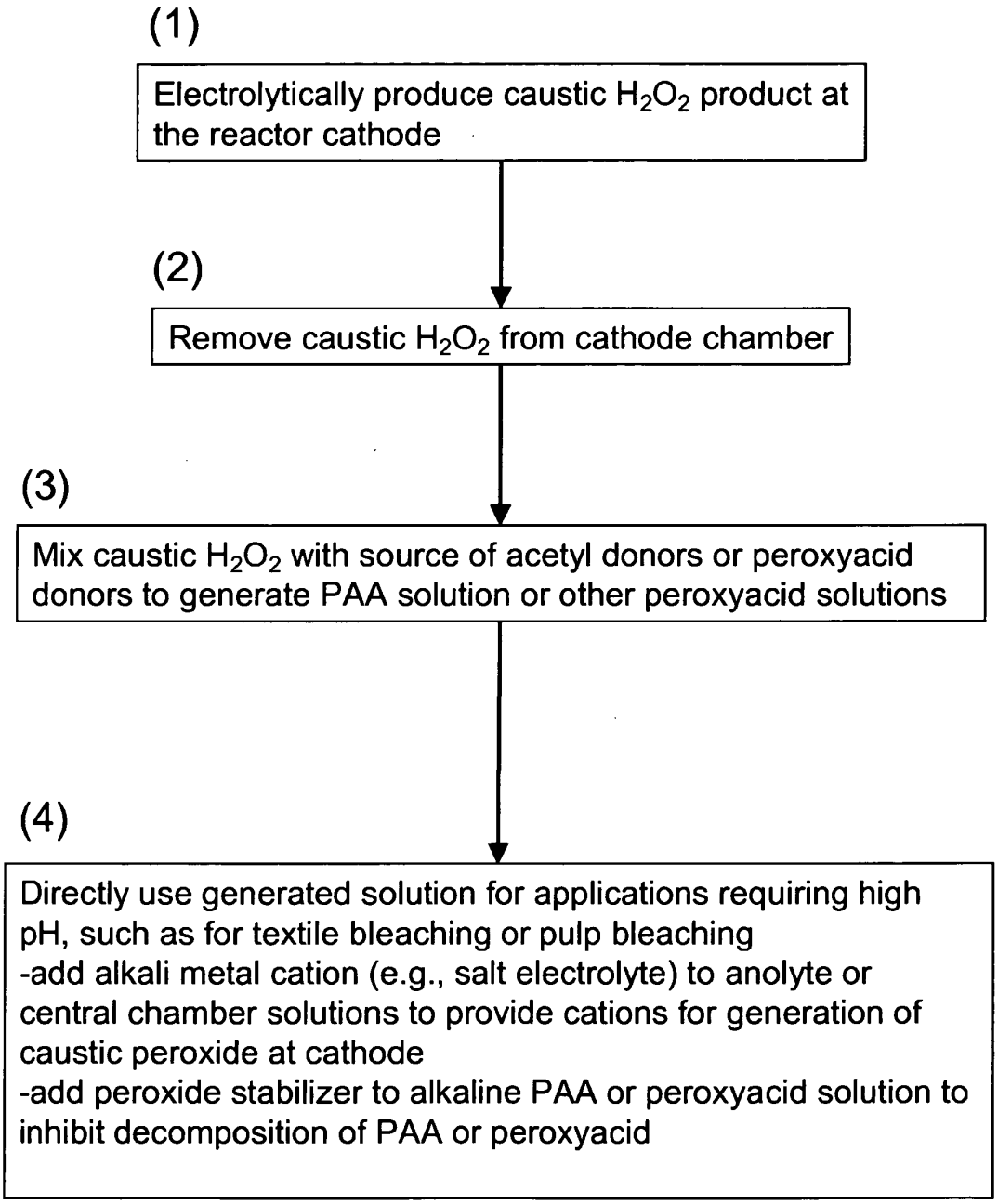

(1)
Electrolytically produce caustic $H_2O_2$ product at the reactor cathode
(2)
Remove caustic $H_2O_2$ from cathode chamber
(3)
Mix caustic $H_2O_2$ with source of acetyl donors or peroxyacid donors to generate PAA solution or other peroxyacid solutions
(4)
Directly use generated solution for applications requiring high pH, such as for textile bleaching or pulp bleaching
-add alkali metal cation (e.g., salt electrolyte) to anolyte or central chamber solutions to provide cations for generation of caustic peroxide at cathode
-add peroxide stabilizer to alkaline PAA or peroxyacid solution to inhibit decomposition of PAA or peroxyacid

**Fig. 2**

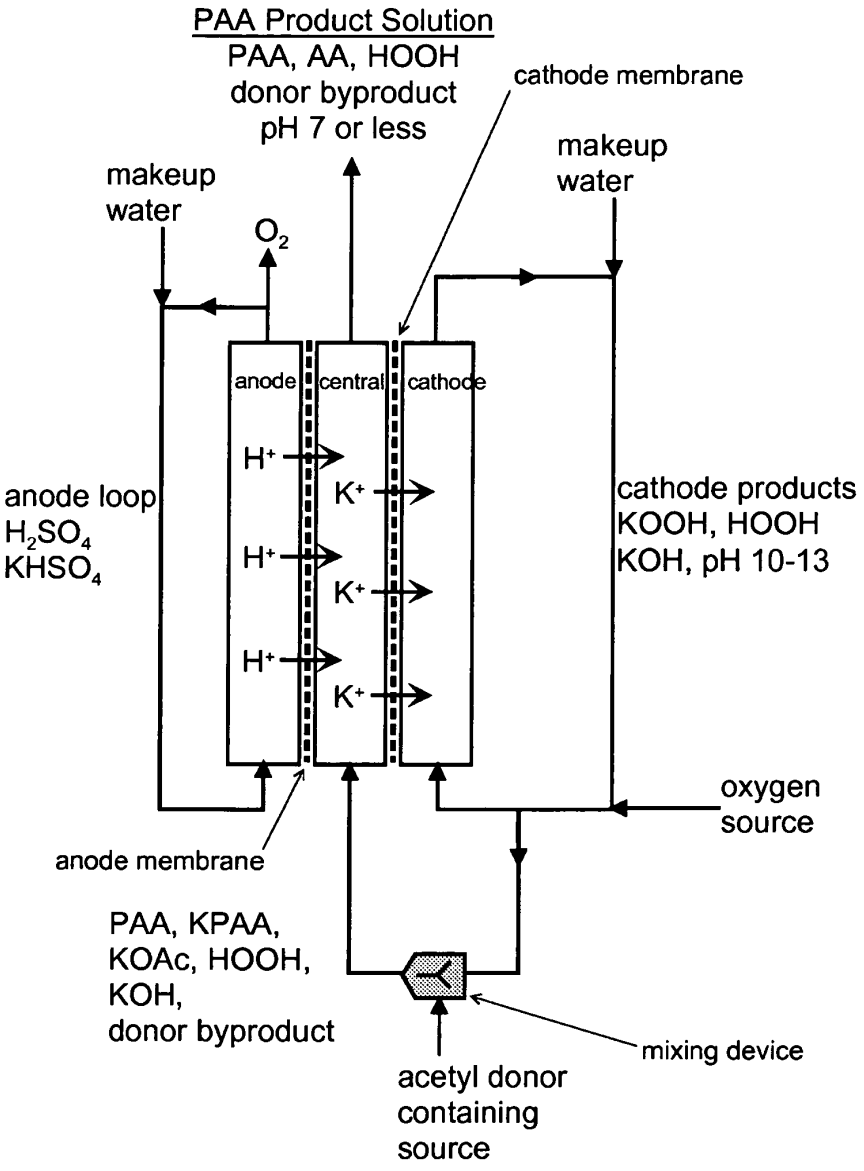

PAA Product Solution
PAA, AA, HOOH
donor byproduct
pH 7 or less
cathode membrane
makeup
water
makeup
water
$O_2$
anode
central
cathode
$H^+$
$K^+$
$H^+$
$K^+$
$H^+$
$K^+$
anode loop
$H_2SO_4$
$KHSO_4$
cathode products
KOOH, HOOH
KOH, pH 10-13
oxygen
source
anode membrane
PAA, KPAA,
KOAc, HOOH,
KOH,
donor byproduct
mixing device
acetyl donor
containing
source

Fig. 3

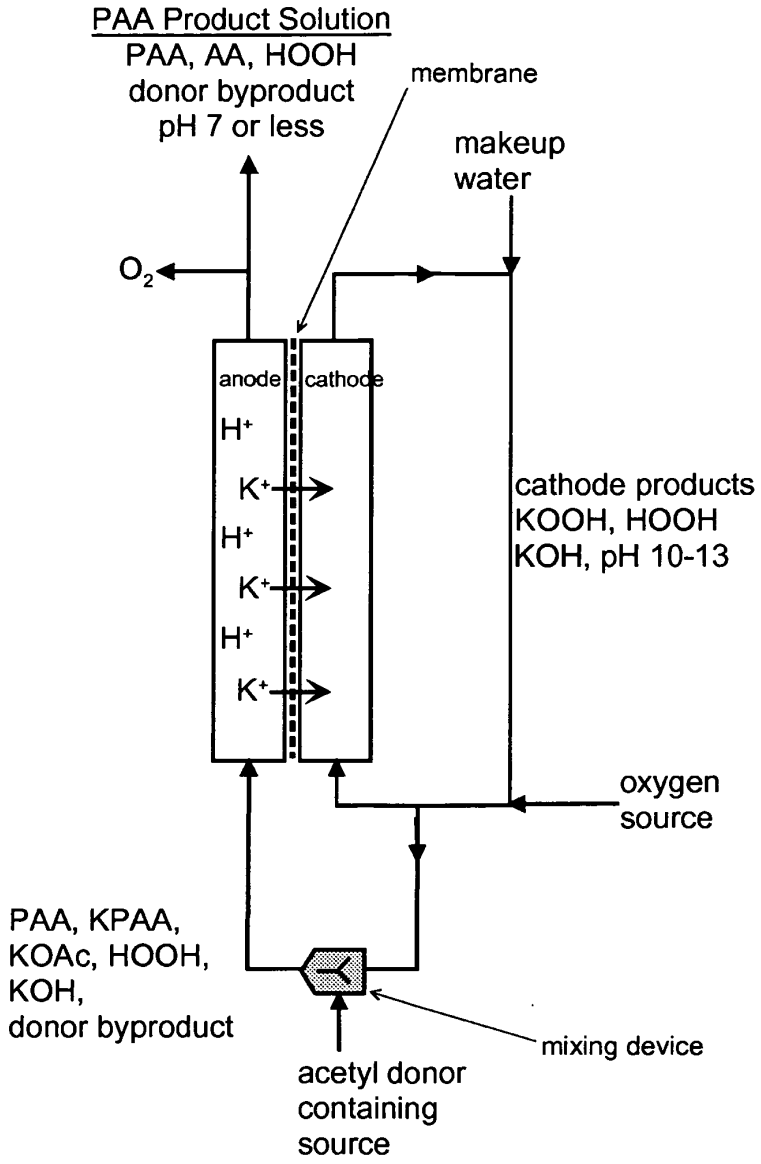

PAA Product Solution
PAA, AA, HOOH
donor byproduct
pH 7 or less
membrane
makeup
water
$O_2$
anode
cathode
$H^+$
$K^+$
$H^+$
$K^+$
$H^+$
$K^+$
cathode products
KOOH, HOOH
KOH, pH 10-13
oxygen
source
PAA, KPAA,
KOAc, HOOH,
KOH,
donor byproduct
mixing device
acetyl donor
containing
source

**Fig. 4**

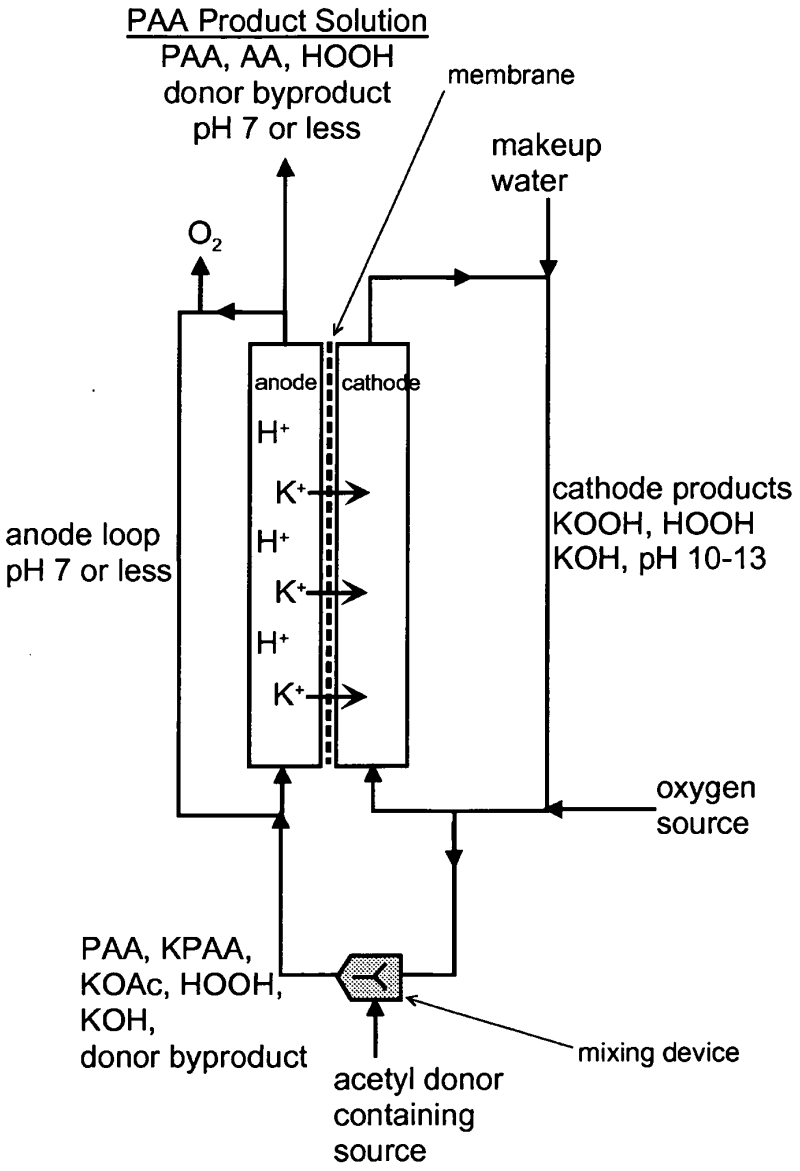

PAA Product Solution
PAA, AA, HOOH
donor byproduct
pH 7 or less
membrane
makeup
water
$O_2$
anode
cathode
$H^+$
$K^+$
$H^+$
$K^+$
$H^+$
$K^+$
anode loop
pH 7 or less
cathode products
KOOH, HOOH
KOH, pH 10-13
oxygen
source
PAA, KPAA,
KOAc, HOOH,
KOH,
donor byproduct
mixing device
acetyl donor
containing
source

**Fig. 5**

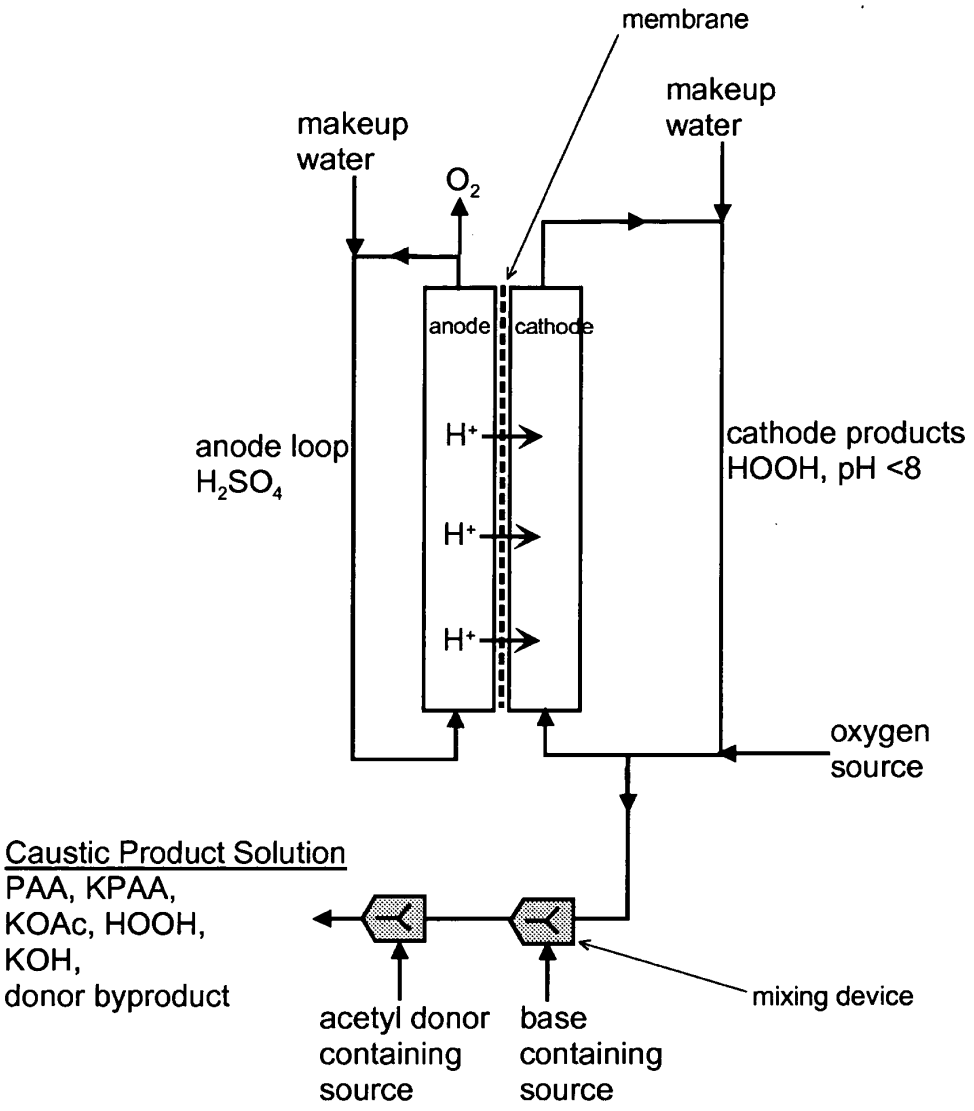

membrane
makeup water
makeup water
$O_2$
anode
cathode
anode loop
$H_2SO_4$
$H^+$
$H^+$
$H^+$
cathode products
HOOH, pH <8
oxygen source
Caustic Product Solution
PAA, KPAA,
KOAc, HOOH,
KOH,
donor byproduct
mixing device
acetyl donor containing source
base containing source

Fig. 6

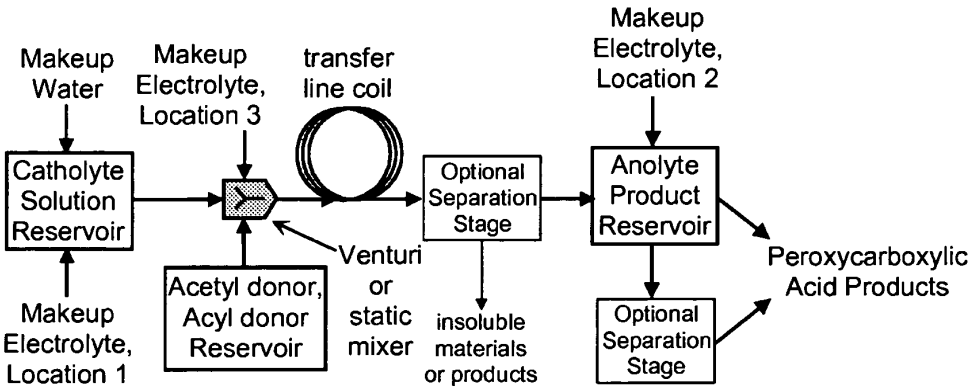

Makeup Water
Makeup Electrolyte, Location 3
transfer line coil
Makeup Electrolyte, Location 2
Catholyte Solution Reservoir
Optional Separation Stage
Anolyte Product Reservoir
Peroxycarboxylic Acid Products
Venturi or static mixer
Acetyl donor, Acyl donor Reservoir
Makeup Electrolyte, Location 1
insoluble materials or products
Optional Separation Stage

Fig. 7

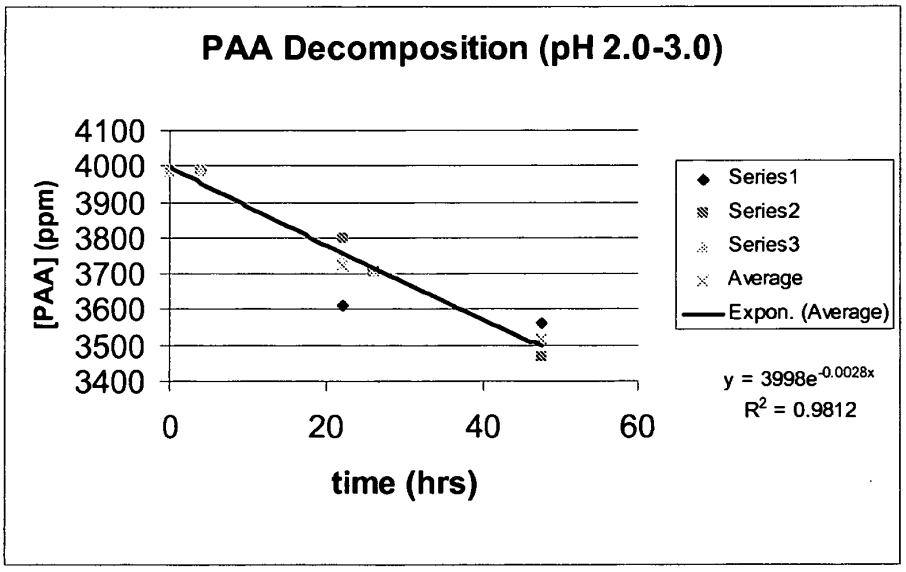

PAA Decomposition (pH 2.0-3.0)
[PAA] (ppm)
4100
4000
3900
3800
3700
3600
3500
3400
0
20
40
60
time (hrs)
Series1
Series2
Series3
Average
Expon. (Average)
y = 3998e-0.0028x
R2 = 0.9812

Fig. 8

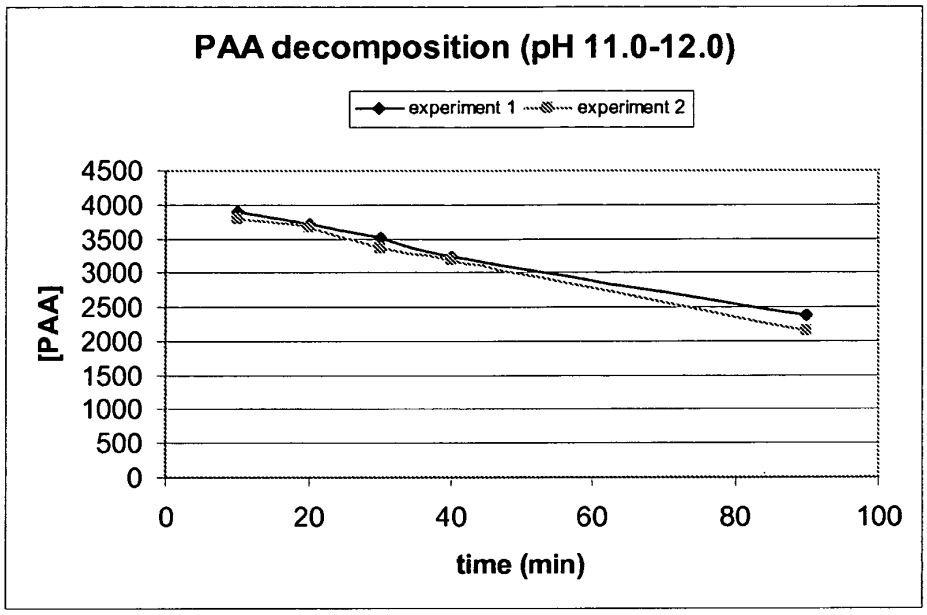

PAA decomposition (pH 11.0-12.0)
experiment 1
experiment 2
[PAA]
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
100
time (min)

Fig. 9

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# Synthesis of peroxyacetic acid using in situ electrogenerated hydrogen peroxide on gas diffusion electrode

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**Abstract**

Peroxyacetic acid (PAA) has been first prepared from acetic acid in the presence of solid superacid, Nafion-H, as a catalyst at ambient temperature and atmospheric pressure using gas diffusion electrode (GDE) as an oxygen cathode. Hydrogen peroxide was electrogenerated by the reduction of oxygen on the GDE and PAA could be produced by a redox reaction between electrogenerated hydrogen peroxide and acetic acid. The continuous operation was carried out to examine the electrolysis performance of the present electrolysis system. The results demonstrate that the system can be continuously operated over one month with the production of PAA of ca. 1.9–2.3 mM.
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*Keywords:* Acetic acid; Gas diffusion electrode; Hydrogen peroxide; Peroxyacetic acid; Nafion-H bead

## 1. Introduction

In the last decade much attention has been being devoted to the application of electrogenerated hydrogen peroxide for the synthesis of organic chemicals, the detoxification and the removal of organics from aqueous solutions [1–11]. An electrochemical method for water treatment, called peroxi-coagulation, using an oxygen diffusion cathode has been developed by Brillas et al. [10]. Recently, Ohtsuka et al. [1,2] has reported the synthesis of phenol from benzene on oxygen reduction cathode with Pd, carbon and Fe catalysts.

Gas diffusion electrodes (GDE) with high performance now are available [12,13], and works on operational parameters such as water mass balance [14] and temperature [15] have been published. With GDE as the cathode, hydrogen peroxide is electrogenerated by the reduction of oxygen and then used for the in situ preparation of peroxyacetic acid (PAA) as demonstrated in this study. PAA is an important reagent in industrial and household bleaching and in disinfection in the food and beverage industries because of its ecological benefits with high reliability [16]. It is synthesized technically in aqueous solution by the reaction of hydrogen peroxide with acetic acid in the presence of sulfuric acid as catalyst [17,18]

$$CH_3COOH + H_2O_2 \overset{H^+}{\leftrightarrows} CH_3COOOH + H_2O \qquad (1)$$

Both PAA and $H_2O_2$ are strong oxidizing agents. The danger and the decrease of activity by self-decomposition are found during transportation and storage. Therefore, the development of new process for the preparation of PAA is of great interest. Recently, we have proposed a method for the preparation of PAA by employing solid superacid, Nafion-H, as a catalyst under ambient conditions [19].

In this communication, we report for the first time an electrochemical method for the preparation of PAA using in situ generated hydrogen peroxide on the GDE cathode in aqueous solution at ambient temperature and

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atmospheric pressure. The factors affecting the cathodic reduction of oxygen to hydrogen peroxide and the formation of PAA will be discussed.

## 2. Experimental

### 2.1. Materials

The solvent, acetic acid used in the present study was of Analar Grade (Kanto Chemical, Japan). The superacid catalyst Nafion-H® beads and Nafion 112 membrane were obtained from DuPont. Organic solvents for the HPLC obtained from Wako Pure Chemical Industry were spectroscopic grade. Solutions were prepared with water obtained from a Millipore Milli-Q system.

### 2.2. Apparatus and procedure

A schematic view of the three-compartment cell used in the preparation of PAA is shown in Fig. 1. The anode and cathode chambers, having a 0.19 $dm^2$ electrolysis area of circular shape, were made of acryl resin. The GDE (geometrical area = 0.19 $dm^2$) cathode was used to electrogenerate hydrogen peroxide and Pt-mesh (80 mesh) electrode was used as the anode. The GDE was prepared in a similar way as reported previously [20] except that no platinum salt as catalyst was loaded. The commercial carbon black (Cabot Corporation, Vulcan XC-72) and poly(tetrafluoroethylene) (PTFE) fine powder (DuPont Mitsui Fluorochemical, 30J) were mixed and stirred in a beaker. The obtained mixture was applied on both sides of a carbon cloth (Zoltek, PWB-3), and then baked at 350 °C in air for 5 min to make a gas permeable conducting matrix. The middle chamber was composed of Nafion-H beads. A Nafion 112 cation permeable membrane was used as solid polymer electrolyte which was mechanically attached with the anode.

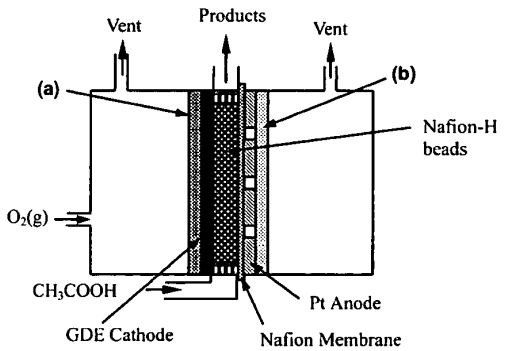



Fig. 1. Schematic drawing of the flow cell used for the preparation of PAA. (a) Porous carbon plate as the current collector for the cathode and (b) porous Ti plate as the current collector for the anode.

Acetic acid (1 M, pH 2.5) was fed into the middle chamber using a metering pump with a constant flow rate. Oxygen gas (99.999%) was fed into the cathode chamber from a gas cylinder at a constant flow rate (10 ml $min^{-1}$). Hydrogen peroxide concentration was determined by titration with permanganate using a standard procedure [16]. The PAA concentration was determined by HPLC consisting of the following components: pump TOSOH CCPM, injector valve, column TOSOH ODS Ts (dimension 150 × 4.6 mm), detector JASCO UV-970, and mobile phase 75% methanol/25% water. The injection volume was 20 μl at a flow rate of 1 ml $min^{-1}$ and the UV detection wavelength was 230 nm.

## 3. Results and discussion

First, it should be noted that no products were obtained under open circuit conditions. The reaction was initiated by shorting the circuit. The reaction mechanism for the preparation of PAA can be presented in the following way:

Anode reaction

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \quad (2)$$

Cathode reaction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

$$CH_3{-}COOH + H_2O_2 \overset{\text{Nafion-H}}{\leftrightarrows} CH_3{-}COOOH + H_2O \quad (4)$$

Both oxygen molecule and proton are generated at the anode. The proton generated is migrated from the anode through the cation exchange membrane to the cathode. The GDE cathode continuously electrogenerates hydrogen peroxide in the acidic media via two-electron reduction of oxygen (Eq. (3)) [4,7] and the electrogenerated hydrogen peroxide can undergo a redox reaction with acetic acid to produce PAA (Eq. (4)). It should be noted here that Nafion-H beads used as a catalyst accelerate the formation of PAA as sulfuric acid catalyzes the formation of PAA from acetic acid and hydrogen peroxide (Eq. (1)) [17,18]. A nucleophilic attack of electrogenerated hydrogen peroxide on protonated acetic acid in the presence of Nafion-H catalyst is a probable cause for the formation of PAA (Eq. (4)) [18].

The effect of current density on the current efficiency for the formation of hydrogen peroxide is shown in Fig. 2. The current efficiency for the cathodic reduction of oxygen to hydrogen peroxide in the electrolytic system was less than ca. 11%. Such a low current efficiency can be attributed to a redox reaction between hydrogen peroxide and acetic acid. Moreover, hydrogen peroxide could undergo decomposition via different chemical and/or electrochemical processes [8]. It is obvious from

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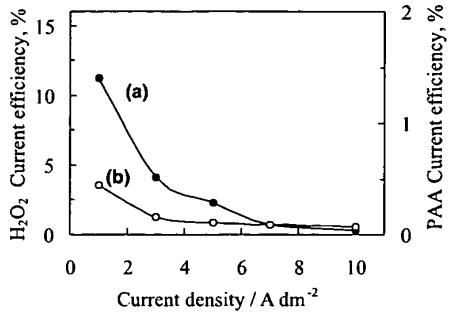



Fig. 2. Effect of current density on the current efficiency for the production of (a) hydrogen peroxide and (b) PAA. Concentration of acetic acid: 1 M; liquid flow rate: 3 ml h$^{-1}$; temperature: 25 °C; oxygen flow rate: 10 ml min$^{-1}$.

Fig. 2 that increasing the current density from 1 to 10 A dm$^{-2}$ decreased the current efficiency for producing hydrogen peroxide from 11% to 1%. This is mainly due to the $H_2$ evolution (side reaction) on the cathode. In addition, further reduction of hydrogen peroxide to water and/or chemical and electrochemical decomposition of hydrogen peroxide significantly occurs as the current density is increased [5,8].

The PAA solutions of 2.63–3.85 mM were found to be prepared when hydrogen peroxide was electrogenerated in 1 M acetic acid, which is considered as the equilibrium concentration of PAA under the preparation conditions used here [18]. Increasing the current density resulted in the formation of PAA with a slightly higher concentration (Table 1). Here it is noted that the concentrations of both hydrogen peroxide and PAA can be precisely controlled by controlling current density. Influence of liquid flow rate on the concentrations of hydrogen peroxide and PAA is also given in Table 1. It was observed that the concentrations of both hydrogen peroxide and PAA decreased with increasing the liquid flow rate at a current density of 5 A dm$^{-2}$, but the molar quantities of both products were increased and thus a higher current efficiency was obtained as the flow rate was increased.

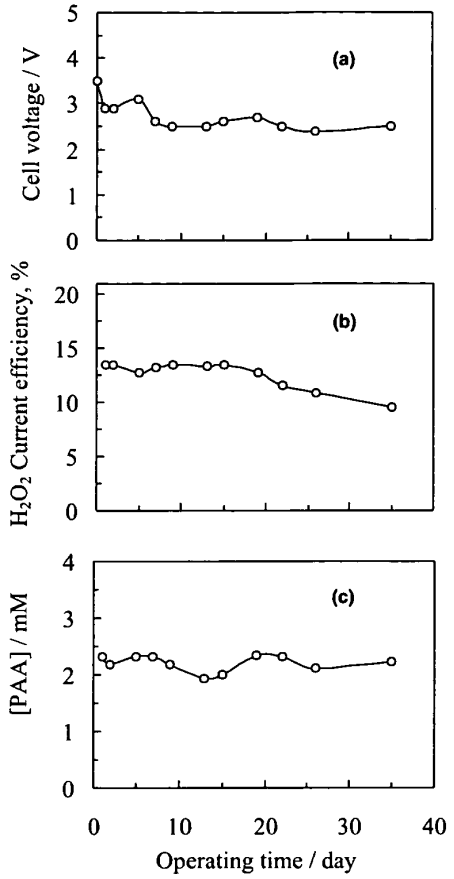



Fig. 3. Stability of (a) cell voltage, (b) $H_2O_2$ current efficiency and (c) PAA concentration in durability test. Current density: 1 A dm$^{-2}$; concentration of acetic acid: 1 M; liquid flow rate: 5 ml h$^{-1}$; oxygen flow rate: 10 ml min$^{-1}$; temperature: 25 °C.

Table 1
Effect of current density on the concentration of PAA solution prepared by electrogenerated $H_2O_2$ at the GDE cathode

| Current density[a] (A dm$^{-2}$) | Cell voltage (V) | Products | |
|---|---|---|---|
| | | $[H_2O_2]$ (mM)[d] | [PAA] (mM)[e] |
| 1 | 3.5 | 132.5 | 2.63 |
| 3 | 4.9 | 147.0 | 2.82 |
| 5 | 5.6 | 135.2 | 3.13 |
| 5[b] | 5.6 | 125.0 | 2.50 |
| 5[c] | 5.6 | 68.2 | 2.10 |
| 7 | 7.0 | 57.3 | 3.52 |
| 10 | 8.2 | 40.0 | 3.85 |

Area of electrode: 0.19 dm$^2$; concentration of acetic acid: 1 M; temperature: 25 °C.
[a] Liquid flow rate was 3 ml h$^{-1}$.
[b] Liquid flow rate was 10 ml h$^{-1}$.
[c] Liquid flow rate was 25 ml h$^{-1}$.
[d] The concentrations were determined by titration method.
[e] The concentrations were determined by HPLC method.

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The results of durability tests of the electrolytic cell at a current density of 1 A $dm^{-2}$ are shown in Fig. 3. The cell voltage was slightly changed (2.5–3.5 V) and current efficiency of hydrogen peroxide formation was 9.5–13.5%. Further, it can be seen from Fig. 3(c) that the present cell can be operated over one month with the production of PAA of ca. 1.9–2.3 mM.

When the current density was increased from 3 to 10 A $dm^{-2}$ at a liquid flow rate of 3 ml $h^{-1}$, the concentration of $H_2O_2$ decreased from 147 to 40 mM, while that of PAA increased from 2.82 to 3.85 mM (Table 1). This result can not be explained only by the acid-catalyzed formation of PAA (Eq. 4). Therefore, it seems also likely that the formation of PAA is initiated by an active oxygen (O*) which might be generated on the cathode surface during the reduction of oxygen [1,2,21,22]. Otsuka et al. [1,2] have explained the partial oxidation of cyclohexane and aromatics on cathodes containing various metal chlorides during $O_2$-$H_2$ fuel cell reactions by assuming the O*-generation similar to that by cytochrome P-450 [21,22].

## 4. Conclusions

In conclusion, the electrochemical synthesis of PAA via the in situ preparation of hydrogen peroxide at the GDE was developed for the first time. The present electrolysis system, in which no mineral acid is needed as catalyst, would be applied for the on-site preparation of PAA. Further studies are needed to clarify the reaction mechanism.

## Acknowledgements

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# Interaction of intrinsic kinetics and internal mass transfer in porous ion-exchange catalysts: Green synthesis of peroxycarboxylic acids

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ABSTRACT

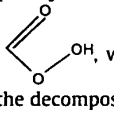
Description of the interactions between intrinsic kinetics and internal mass transfer is one of the central issues in chemical reaction engineering. A general model was developed, comprising the kinetic and mass transfer effects in porous particles reacting in batch reactors. The catalyst particle size distribution was included in the model. A numerical algorithm and software was developed to solve the model for simulation and parameter estimation purposes. The model was applied to an industrially relevant case of green chemistry: synthesis of peroxycarboxylic acids from carboxylic acids and hydrogen peroxide. Due to the potential industrial applications, the present study was focused on the acetic and propionic acid perhydrolysis. The concentrations in the bulk phase and inside the catalyst particles were predicted by the model. It turned out that the smallest ion-exchange resin particles operated under kinetic control, whereas the largest particles (higher than 300 μm) are influenced by diffusional limitation. Thus the combined effect of reaction and diffusion along with the particle size distribution are essential ingredients in the model.
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## 1. Introduction

The environmental impact and the safety aspects for the production of chemicals are the two main issues to ensure the sustainability of industrial production. Preventing the formation of waste products, suppressing the energy consumption, designing safer process, utilizing non-toxic and non-hazardous chemicals, and optimizing the productivity are the main concerns of all the chemical companies. The concept of "Green Chemistry" introduced in the 1990s has provided methods and tools to take into account these issues for the scientific and industrial community. Synthesis of peroxycarboxylic acid can be regarded as a textbook example of the philosophy.

The pioneering research of the laboratory-scale synthesis of peroxycarboxylic acids began by D'Ans and Frey (1914), and the industrial production started around 75 years ago. However, since that time, the patents concerning the production of peracids still recommended homogeneous catalysts, such as sulphuric acid; which is recirculated to the process. The consequences of using sulphuric acid are corrosion of the equipment, setup of an energy-consuming distillation system for the catalyst separation, and threat to the environment. In addition, impurities of the feed are enriched in the recycling catalyst solution.

The application of peroxycarboxylic acids (Kitis, 2004) as a disinfectant is widely spread in different industries: alimentary manufactures, pharmaceutical industry, dairy manufacture and in sewage treatment to disinfect wastewaters. Peroxycarboxylic acids are used as oxidizing agents in fine chemical industry for instance in epoxidation of olefins, Baeyer–Villiger reaction, or oxidation of thioether. Another area of application is in textile, pulp and paper industries as a decoloring agent.

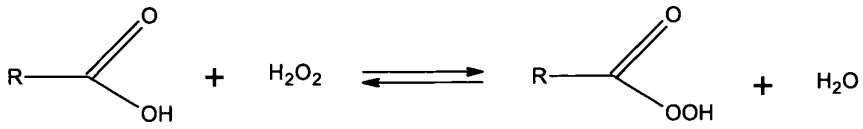
The properties of peroxycarboxylic acids are based on their exotic functional group , which gives them their oxidative power. Furthermore, the decomposition products of the compounds are eco-friendly (Musakka et al., 2006; Leveneur et al., 2007; Zhao et al., 2008). For instance, the use of peroxyacetic acid for the bleaching of wood pulp assures a total chlorine-free process. From the viewpoint of safety, an advantage is that peroxycarboxylic acids can be produced on-site, and the handling of them is convenient.

Several routes for peroxycarboxylic acids (PCA) synthesis are available: oxidation of the parent aldehyde (Phillips et al., 1958) or carboxylic acid (Cantieni, 1937). In this study, a "green" oxidation of the parent carboxylic acid with aqueous hydrogen peroxide is used,

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**Scheme 1.** Synthesis of PCA from the corresponding carboxylic acid and hydrogen peroxide.

following the recommendation of Noyori (2005). Scheme 1 represents the reversible reaction of perhydrolysis of carboxylic acid.

Due to a slow kinetics, an acid catalyst is needed to increase the velocity of this reaction. Sulphuric acid is the most common mineral acid used. A greener way is to utilize heterogeneous catalysts, e.g., cation exchange resins. Based on the previous paper from our group (Leveneur et al., 2009), the use of Amberlite IR-120, as a heterogeneous catalyst, is a feasible alternative to homogeneous catalysis.

Few articles deal with the kinetics (Dul'neva and Moskvin, 2005) and modelling (Zhao et al., 2007) of peroxyacetic or peroxypropionic acid synthesis (Leveneur et al., 2008) catalyzed by sulphuric acid. Kinetic modelling of peroxyacetic acid catalyzed by Amberlite IR-120 was carried out by Musante et al. (2000). The objective of the present communication is to provide a comparison between homogeneous and heterogeneous catalysis system. To quantify this comparison by determining the parameters which govern the process, kinetic models corresponding for both catalytic systems were developed.

Because of the industrial practise and potential applications, two different peroxycarboxylic acids were studied: peroxyacetic acid (PAA) and peroxypropionic acid (PPA). Indeed, peroxyacetic acid is the most common peroxycarboxylic acids used industrially. However, PPA is more stable than PAA; and, furthermore propionic acid is less volatile ($t_B = 141\,^{\circ}C$) than acetic acid ($t_B = 118.1\,^{\circ}C$). The shortest chain peroxycarboxylic acid, peroxyformic acid is used to epoxidize unsaturated vegetable oils, but this compound should be prepared in situ for safety reasons.

Kinetic modelling of the carboxylic acids perhydrolysis reaction by using a homogeneous catalyst was inspired from the previous study (Leveneur et al., 2008). In case of heterogeneous catalysis, the particle size distribution (PSD) of the catalysts was included in the kinetic model to take into account the internal diffusion phenomenon, as Wärnå et al. (2002) has done previously.

## 2. Experimental section

### 2.1. Apparatus and experimental procedures

All experiments were performed in a 250 ml jacketed glass reactor vessel. The reactor was equipped with a mechanical agitator and a temperature probe. Water was pumped through the outer jacket of the vessel to control the temperature of the reaction mixture. A pitched blade impeller (PTFE coated) was used to ensure vigorous mixing (the agitation speed was adjusted at 250 rpm) during the reaction.

A reflux condenser was attached to the top of the reactor (adjusted at 0 °C) to avoid the loss of volatile liquid-phase compounds. In case that decomposition of peroxycarboxylic acid or $H_2O_2$ might appear, an inert gas (Helium, AGA, 99.996%) was introduced to the reactor through one of the necks in order to avoid accumulation of oxygen in the gas phase.

To prevent the contamination induced by alkaline and metal components, which initiate the catalytic decomposition of peroxycarboxylic acid and hydrogen peroxide, all parts of the reactor system being in contact with the reaction solution were washed with hydrochloric acid followed by another washing, with a phosphate-free detergent solution.

**Table 1**
Experimental matrix for the homogeneous catalysis system.

| | |
|---|---|
| Reaction temperature | 30–60 °C |
| Rotation speed | 250 rpm |
| $[AA]_0$ | 5.15–9.00 mol $l^{-1}$ |
| $[PA]_0$ | 1.80–6.50 mol $l^{-1}$ |
| $[H_2O_2]_0$ | 1.95–7.00 mol $l^{-1}$ |
| $[H_2O]_0$ | 16.80–40.70 mol $l^{-1}$ |
| $[H_2SO_4]_0$ | 0.0–1.41 mol $l^{-1}$ |

**Table 2**
Experimental matrix for the heterogeneous catalysis system.

| | |
|---|---|
| Reaction temperature | 30–60 °C |
| Rotation speed | 250 rpm |
| $[AA]_0$ | 5.60–9.30 mol $l^{-1}$ |
| $[PA]_0$ | 4.95–7.40 mol $l^{-1}$ |
| $[H_2O_2]_0$ | 4.40–7.40 mol $l^{-1}$ |
| $[H_2O]_0$ | 18.35–29.10 mol $l^{-1}$ |
| Catalyst (Amberlite) loading on dry basis | 0.00–98.75 g $l^{-1}$ |

At the first stage, carboxylic acids (propionic acid: Acros, 99 wt% and acetic acid: J.T.Baker 99–100 wt%) and the catalyst (sulphuric acid: J.T.Baker 95–97 wt% or Amberlite IR-120 Aldrich) were mixed together in the reactor. As the desired reaction temperature was reached, preheated hydrogen peroxide solution (Merck, 30 wt%) was added through a dropping funnel. At the time "zero" the required amount was introduced into the reactor.

To obtain a reliable kinetic model for the perhydrolysis of carboxylic acids, the experimental parameters in case of the homogeneous (Table 1) and heterogeneous catalyst (Table 2) were used.

### 2.2. Analytical methods

Samples were withdrawn from the reaction mixture (around 2.4 g) with a plastic syringe (to avoid contamination of the solution by trace of metals) and were analysed by the method of Greenspan and Mackellar (1948). The change of the liquid volume was taken into account, since the liquid volume was diminished during the reaction because of sampling. The concentration of hydrogen peroxide was determined by titration with a standard solution of ammonium cerium sulphate (0.1 N). The concentrations of carboxylic and peroxycarboxylic acids were determined by titration with an automatic titrator (Metrohm 751 GPD Titrino) using a standard solution of sodium hydroxide (0.2 N).

### 2.3. Catalyst properties and characterization

The properties of the Amberlite IR-120 are summarized in Table 3. It is a cation exchange resin with a styrene-divinyl benzene matrix bearing sulphonic acid groups, which were used in the form of beads.

Different pretreatments of Amberlite IR-120 were carried to check their potential influence on the kinetics of the reaction, namely drying at 70 and 90 °C for 48 h in an oven, and at 70 °C under vacuum (16 mbar) for 48 h.

The concentration of the acid sites on the catalyst was determined by a conventional titration method (Xu and Chuang, 1997).

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Around 0.5 g of the catalyst sample was added to about 50 ml of NaCl solution (200 g/l) and stirred. The ion exchange between $H^+$ and $Na^+$ was allowed to proceed for 24 h. The mixture was then titrated with a 0.1 N NaOH solution. To have a complementary method to determine the capacity of the resins, an elementary analysis of the sulphur content was carried out by a ThermoQuest Flash EA1112 Series elemental, which oxidizes the sample and measures the gas as a gas chromatography.

A study of the particle size distribution was done on the pretreated resins (dried at 99 °C) by the classical sieving method, and on the swelled resins in water at room temperature using a Malvern 2600 model. The measurement of the particle size distribution by the Malvern instrument is based on a He–Ne laser diffraction system.

## 3. Catalyst characterization results

### 3.1. Particle size distribution

The exchange capacity of the resin, determined by the titration method, is equal to 4.7 meq/g (on dry basis). This value is an average value of three different measurements.

By assuming that all the sulphur determined by the elementary analysis corresponds to the $-SO_3H$ group, the average capacity value was calculated to be equal to 4.4 meq/g (on dry basis).

By using the titration method, Musante et al. (2000) have found a capacity equal to 4.5 meq/g (on dry basis). The exact value of the Amberlite IR-120 capacity is difficult to determine, due to experimental errors, the sensitivity of the elementary analysis and the non-ideality of the titration mixture. Moreover, the behaviour of these resins in our reaction mixture might be different. Then, it is reasonable to assume that the capacity value fluctuates between 4.4 and 4.7 meq/g (on dry basis). In the modelling, the value of the capacity was assumed to be equal to 4.7 meq/g (on dry basis).

By sieving the pretreated resin, the following distribution was found:

- the particle percentage with a diameter higher than 500 μm is equal to 63.6%, while
- the particle percentage with a diameter lower than 500 μm is equal to 36.4%.

The particle size distribution of the swelled resin in water obtained by the Malvern 2600 measurement is displayed in Fig. 1.

From these results, one can notice a swelling effect between the dried particles and the particles in water. The concentration of particles with a diameter higher than 500 μm in water has increased by ca. 16% compared to dry particles.

According to Musante et al. (2000), in case of the perhydrolysis of acetic acid over Amberlite IR-120, water is more strongly sorbed than either acetic acid or hydrogen peroxide, and the resin swelling is thus much higher in water than in acetic acid. However, the difference in the kinetics and thermodynamic occurs only between the experiments carried out with homogeneous and heterogeneous catalysts, and when the difference in the sorption behaviour of the reactants is significant.

For the sake of simplicity, the swelling effect in water is assumed to be the same as of the reaction mixture. Indeed, water is the solvent in the experimental condition.

**Table 3**
Properties of Amberlite IR-120 given by the manufacturer.

| Amberlite IR-120 | |
|---|---|
| Polymer type | Gel |
| Cross linking, % | 8 |
| Moisture content, % mass | 45 |
| Capacity by dry weight, meq/g | 4.4 |
| Native particle size range, mm | 0.3–1.2 |

### 3.2. Influence of the pretreatment of Amberlite IR-120

The main purpose of the pretreatment of the commercial Amberlite IR-120 is to release the native water from the resins. Amberlite IR-120 resins pretreated at different temperatures and pressures were tested. The aim was to inspect, whether the internal structure of the resin varies with different pretreatment methods.

From Fig. 2 one can notice that there is no influence of the nature of the pretreatment on the kinetics of propionic acid perhydrolysis, which implies that the different pretreatments modify the internal

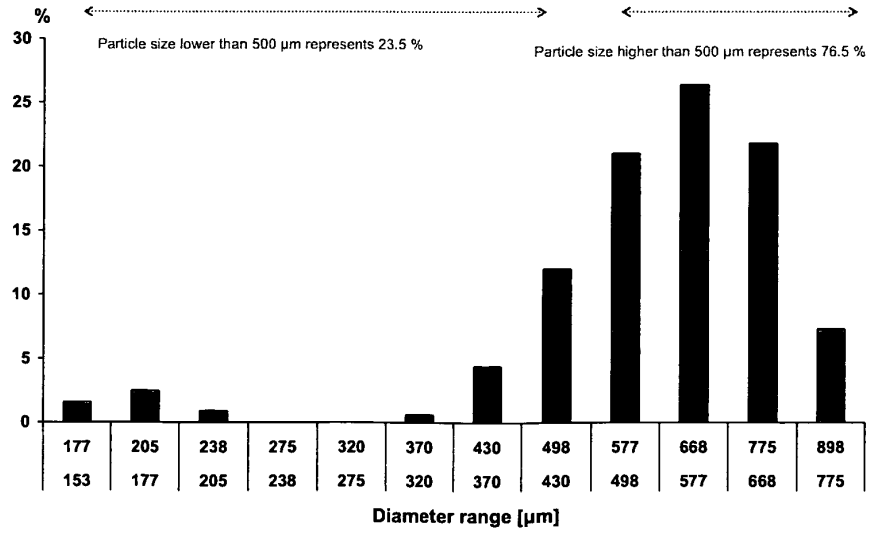



**Fig 1.** The particle size distribution of the Amberlite IR-120 measured by Malvern 2600.

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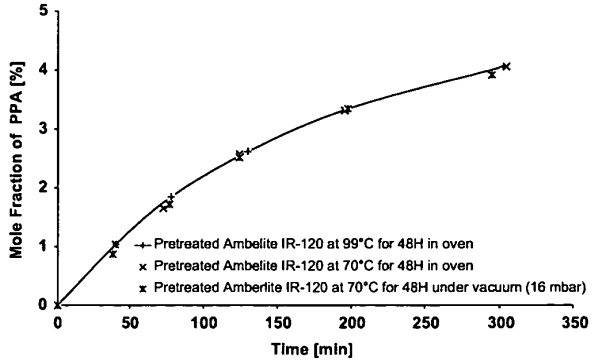



**Fig 2.** The influence of the catalyst (Amberlite IR-120) pretreatment on the mole fraction of peroxypropionic acid at 40 °C and catalyst loading of 49 g l$^{-1}$.

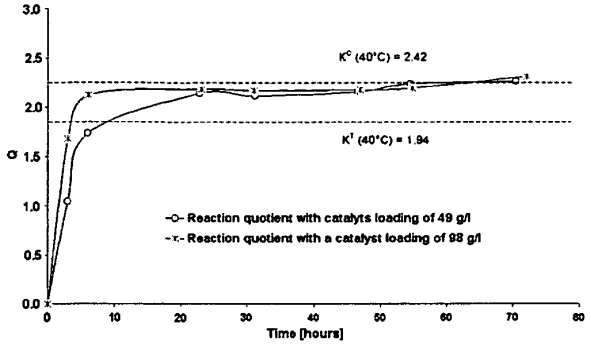



**Fig 3.** Equilibrium experiments for the perhydrolysis of propionic acid at 40 °C.

catalyst structure in the same way. From a previous study (Leveneur et al., 2009), it was found that there is a difference in the kinetics for the experiments carried out with native Amberlite IR-120 and pretreated Amberlite IR-120.

## 4. Equilibrium analysis

### 4.1. Homogeneous catalysis

The non-ideality in the propionic acid perhydrolysis catalyzed by sulphuric acid was described previously (Leveneur et al., 2008). This non-ideality is mainly due to the presence of the strong electrolyte; therefore, a parameter $\delta$ was introduced to describe it.

A linear relationship between $K^C$ (defined as the concentration ratio $[PCA]_{eq}[H_2O]_{eq}/[CA]_{eq}[H_2O_2]_{eq}$) and $[H_2SO_4]_0$ was established as

$$K^C = \delta^*[H_2SO_4]_0 + K^T \tag{1}$$

The true thermodynamic constant $K^T$ follows the law of Van't Hoff:

$$\frac{d \ln K^T}{dT} = \frac{\Delta H_r^0}{RT^2} \tag{2}$$

where $\Delta H_r^0$ stands for the standard reaction enthalpy change. Assuming that $\Delta H_r^0$ is independent of $T$, integration of Eq. (2) from a particular temperature $T_{ref}$ to an arbitrary temperature $T$ leads to

$$\ln \frac{K^T}{K_{ref}^T} = \frac{-\Delta H_r^0}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \tag{3}$$

To determine the standard reaction enthalpy change $\Delta H_r^0$ of the acetic acid perhydrolysis reaction, the protocol described in the previous article (Leveneur et al., 2008) was applied. The standard enthalpy change of the reaction ($\Delta H_r^0$) and $K_{ref}^T$ were estimated separately, namely these thermodynamic parameters were determined by carrying out some experiments for longer reaction times (around 20 h) to reach the equilibrium composition. The results of the modelling will be discussed in Section 7.1.

### 4.2. Heterogeneous catalysis

Fig. 3 represents the reaction quotient $Q = [PPA] * [H_2O]/[PA] * [H_2O_2]$ versus time for two experiments carried out with two different catalysts loadings.

The water concentration $[H_2O]$ was determined by adding the initial water concentration and the concentration of PPA formed (the experiments were always commenced with a PPA-free solution). The limiting value of $Q$ obtained from Fig. 3 is 2.42.

Based on Eq. (3) and the data from the previous article (Leveneur et al., 2008), the value of the true equilibrium constant at 40 °C is equal to 1.94.

From Fig. 3, one can notice that there is a difference between the true thermodynamic constant $K^T$ and the equilibrium constant $K^C$, which implies that even in presence of a solid acid catalyst, the reaction mixture is slightly non-ideal. However, the change of the catalyst loading does not affect the equilibrium constant $K^C$.

The equilibrium constant $K^C$ is defined as: $K^C = K^T/K^\gamma$, where $K^\gamma$ represents the equilibrium constant calculated based on the activity coefficients. For the sake of simplicity, $K^\gamma$ was assumed to be constant in the temperature range 30–60 °C, and, the constant $K^C$ was calculated as

$$K^C = \frac{K^T}{K^\gamma} = \frac{K^T}{0.8}$$

where the value of 0.8 was calculated based on Fig. 3, and $K^T$ was determined from Eq. (3).

## 5. Mechanism and kinetic equations

### 5.1. Homogeneous catalysis

A detailed description of the kinetic equations can be found in the previous paper (Leveneur et al., 2008). Based on the experimental results, the following simplified mechanism was proposed (Fig. 4). Protolysis equilibria play a central role in the mechanism. The last steps (VI–VII) describe the synthesis reaction itself.

By applying the quasi-equilibrium hypothesis on the rapid proton transfer reaction VI and by defining reaction VII as the rate limiting, the rate expression becomes:

$$r = r_{VII} = k_{VII} * K_{VI}^C * \frac{[H_3O^+]}{[H_2O]} * \left([RCOOH] * [H_2O_2] - \frac{1}{K_{VI}^C * K_{VII}^C} * [RCO_3H] * [H_2O]\right) \tag{4}$$

The term $K_{VI}^C * K_{VII}^C$ represents the global equilibrium constant for the reaction denoted by $K_{hom}^C$, which is estimated by Eqs. (1) and (3). The term $k_{VII} * K_{VI}^C$ is denoted by a merged constant $k_{hom}$.

Finally, the reaction rate can be expressed by the following expression:

$$r = k_{hom} * \frac{[H_3O^+]}{[H_2O]} * \left([CA] * [H_2O_2] - \frac{1}{K_{hom}^C} * [PCA] * [H_2O]\right) \tag{5}$$

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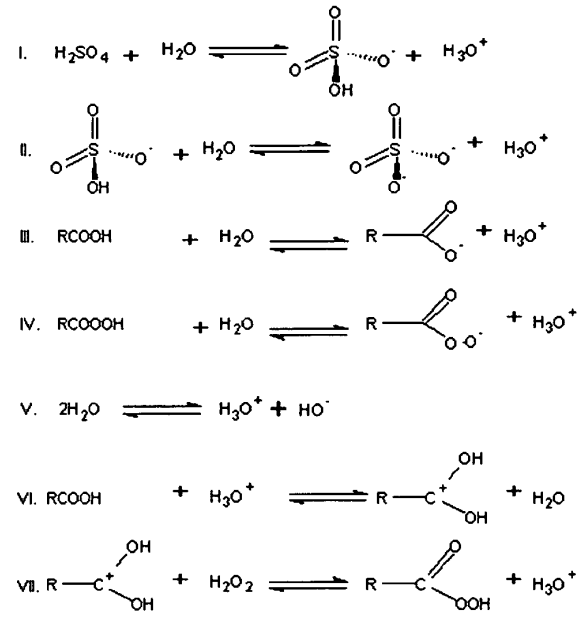



**Fig 4.** Simplified mechanism for peroxycarboxylic acid synthesis by sulphuric acid in aqueous media.

The hydroxonium ion concentration $[H_3O^+]$ was determined based on the electroneutrality principle and the protolysis equilibria, and after some simplifications, the concentration can be calculated from:

$$[H_3O^+] = \frac{1}{2} * [H_2SO_4]_0 + \sqrt{\frac{[H_2SO_4]_0^2}{4} + 2 * K_{II}^C * [H_2SO_4]_0 * [H_2O] + K_{III}^C * [H_2O] * [CA]} \quad (6)$$

where the mathematical expressions for the dissociation constants $K_{II}^C$ and $K_{III}^C$ were found from the literature (Knopf et al., 2003; Sue et al., 2004).

### 5.2. Heterogeneous catalysis

Several articles treat the carboxylic acid esterification (Altiokka and Çitak, 2003; Liu and Tan, 2001) or hydrolysis of esters (Altiokka, 2007) catalyzed by cation exchange resins as an Eley–Rideal mechanism. This mechanism implies that one reactant molecule adsorbs on the surface.

According to several studies (Dul'neva and Moskvin, 2005; Zhao et al., 2007; Leveneur et al., 2008; Musante et al., 2000), the protonation of the carbonyl group is the key step, which it is a strong argument to assume that the carboxylic acid adsorbs on the active site, and hydrogen peroxide molecule reacts from the bulk phase. However, the protolysis of the carboxylic acid and the adsorption of water on the active sites (Altiokka, 2007) should be taken into account. The following mechanism (Fig. 5) is proposed.

From Fig. 5, it should be noticed that the mechanism can be divided into two different parts: the homogeneous part due to the protolysis of carboxylic acids producing hydroxonium ions, which act catalytically; and the heterogeneous part due to the sulphonic groups on the resins. The peroxycarboxylic acid is a much weaker acid than the corresponding carboxylic acid. Therefore, the acid-catalytic effect of the peroxycarboxylic acid is not included in the scheme. The total rate $r_{tot}$ of the reaction is the sum of the rates of the reactions 2 and 6, in Fig. 5.

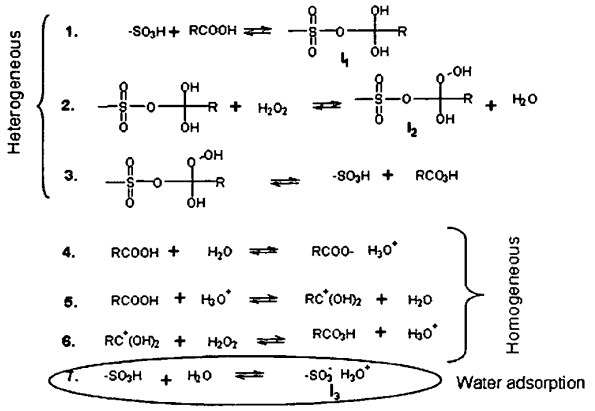



**Fig 5.** Simplified mechanism for peroxycarboxylic acid synthesis by Amberlite IR-120 in aqueous media.

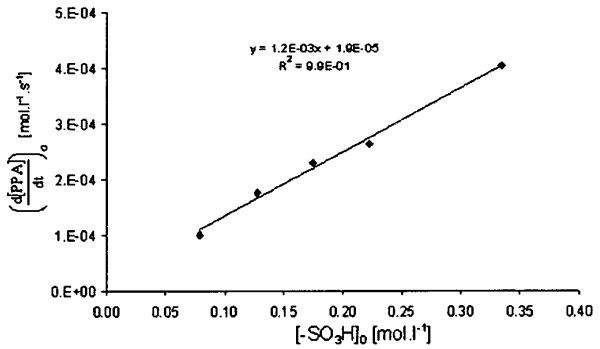



**Fig 6.** Influence of the loading catalyst on the perhydrolysis of propionic acid at 50 °C.

Fig. 6 represents the initial rates of peroxypropionic acid formation $(d[PPA]/dt)_0$ plotted versus the active site concentration $[-SO_3H]$ (mol l$^{-1}$), which is the apparent Brønsted acid concentration, i.e., the number of sulphonic groups bearing by the solid catalyst present per litre of solution. From the kinetic model for the synthesis of peroxypropionic acid using the homogeneous catalyst (Leveneur et al., 2008), in the absence of sulphuric acid the initial rate of formation of PPA is equal to $2.15\times10^{-5}$ mol l$^{-1}$ s$^{-1}$ at 50 °C, which is closer to $1.87\times10^{-5}$ mol l$^{-1}$ s$^{-1}$ given by Fig. 6.

### 5.3. Kinetic expressions for heterogeneous catalysis (Amberlite IR-120)

For the homogeneous part of the system, the quasi-equilibrium hypothesis was applied to the reversible proton donor (reaction 5). By noting the ratio $k_{+5}/k_{-5}$ equal to $K_5^C$, the concentration of the intermediate $RC^+(OH)_2$ is obtained from

$$[RC^+(OH)_2] = \frac{K_5^C * [RCOOH] * [H_3O^+]}{[H_2O]} \quad (7)$$

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Concentrations of carboxylate anions and hydroxonium ions are equal; then, the concentration of $[H_3O^+]$ can be obtained from

$$[H_3O^+] = \sqrt{K_4^C[RCOOH][H_2O]} \tag{8}$$

The rate-determining step for the homogeneous system is the reversible reaction 6, and the rate $r_{hom}$ can now be expressed as

$$\begin{aligned} r_{hom} = r_6 &= k_{+6} * [RC^+(OH)_2] * [H_2O_2] - k_{-6} * [RCO_3H] * [H_3O^+] \\ &= \frac{k_{+6} * K_5^C * \sqrt{K_4^C * [RCOOH] * [H_2O]}}{[H_2O]} \\ &\quad * \left( [RCOOH] * [H_2O_2] - \frac{1}{K_5^C K_6^C} * [RCO_3H] * [H_2O] \right) \end{aligned} \tag{9}$$

where the equilibrium constant $K_6^C$ is equal to the ratio $k_{+6}/k_{-6}$. The products $k_{+6} * K_5^C$ and $K_5^C * K_6^C$ are denoted by the merged constants $k_{hom}$ and $K_{hom}^C$, respectively. Then, Eq. (9) becomes:

$$\begin{aligned} r_{hom} = r_6 &= \frac{k_{hom}\sqrt{K_4^C * [RCOOH] * [H_2O]}}{[H_2O]} \\ &\quad * \left( [RCOOH] * [H_2O_2] - \frac{1}{K_{hom}^C} * [RCO_3H] * [H_2O] \right) \end{aligned} \tag{10}$$

For the heterogeneous part of the system, the quasi-equilibrium hypothesis is applied on reactions 1, 3 and 7, with the corresponding adsorption constants $K_1^C$, $K_3^C$ and $K_7^C$. Then, the concentration of sulphonic group can be expressed as

$$[-SO_3H] = \frac{[-SO_3H]_0}{1 + K_1^C * [RCO_2H] + K_3^C * [RCO_3H] + K_7^C * [H_2O]} \tag{11}$$

where $[-SO_3H]_0$ is the initial sulphonic group concentration.

The rate-determining step for the heterogeneous system is the reversible reaction 2, and the rate $r_{het}$ can be expressed as

$$\begin{aligned} r_{het} = r_2 &= k_{+2} * [I_1] * [H_2O_2] - k_{-2} * [I_2] * [H_2O] \\ &= \frac{k_{+2} * K_1^C * [-SO_3H]_0}{1 + K_1^C * [RCO_2H] + K_3^C * [RCO_3H] + K_7^C * [H_2O]} \\ &\quad * \left( [RCO_2H] * [H_2O_2] - \frac{K_3^C}{K_1^C * K_2^C} * [RCO_3H] * [H_2O] \right) \end{aligned} \tag{12}$$

The terms $k_{+2} * K_1^C$ and $K_3^C/K_1^C * K_2^C$ are denoted by the lumped constants $k_{het}$ and $K_{het}^C$, respectively. Then, Eq. (12) becomes:

$$\begin{aligned} r_{het} = r_2 &= \frac{k_{het} * [-SO_3H]_0}{1 + K_1^C * [RCO_2H] + K_3^C * [RCO_3H] + K_7^C * [H_2O]} \\ &\quad * \left( [RCO_2H] * [H_2O_2] - \frac{1}{K_{het}^C} * [RCO_3H] * [H_2O] \right) \end{aligned} \tag{13}$$

By adding Eqs. (10) and (13), the total rate combining homogeneous and heterogeneous part is

$$\begin{aligned} r_{tot} &= r_{hom} + r_{het} \\ &= \left[ \frac{k_{hom} * \sqrt{K_4^C * [RCO_2H] * [H_2O]}}{[H_2O]} \right. \\ &\quad \left. + \frac{k_{het} * [-SO_3H]_0}{1 + K_1^C * ([RCO_2H] + [RCO_3H]) + K_7^C * [H_2O]} \right] \\ &\quad * \left[ [RCO_2H] * [H_2O_2] - \frac{1}{K^C} * [RCO_3H] * [H_2O] \right] \end{aligned} \tag{14}$$

The main assumption is that the global equilibrium constants in case of the homogeneous system $K_{hom}^C$ and in case of the heterogeneous system $K_{het}^C$ are equal. Due to a similar structure of the peroxycarboxylic acid and the corresponding carboxylic acid, the adsorption coefficients $K_1^C$ and $K_3^C$ were approximated to be equal.

The values of $k_{hom}$ were estimated in the previous work (Leveneur et al., 2008) for the perhydrolysis of propionic acid, and estimated by the kinetic model for the perhydrolysis of acetic acid by sulphuric acid. The value of $K_4^C$ was calculated based on the equation from Sue et al. (2004). Altiokka (2007) has investigated the kinetics of benzaldehyde dimethyl acetal hydrolysis over Amberlite IR-120, which is the same catalyst as used in this study. The adsorption equilibrium constant related to water was calculated to be $K_{water} = \exp(1296/T - 4.4)$. The value for the adsorption coefficient of water $K_7^C$ was calculated based on the equation developed by Altiokka (2007). In the kinetic modelling, the heterogeneous rate constant $k_{het}$ and the adsorption coefficient $K_1^C$ were estimated with regression analysis.

## 6. Mass transfer effect in case of the heterogeneous catalyst

### 6.1. Experimental verification of mass transfer

From a previous study (Leveneur et al., 2009), it has been demonstrated that there is no external mass transfer limitation in the range 250–600 rpm for the perhydrolysis of propionic acid catalyzed by pretreated Amberlite IR-120.

However, by sieving the pretreated Amberlite IR-120 particles into two different size fractions, i.e., lower and higher than 500 μm; the presence of internal mass transfer limitation in the beginning of the reaction was confirmed (Fig. 7 and Table 4). One should keep in mind that the particle diameter ($d_p$) corresponds to the dried particles, and not the swollen particles in the reaction mixture.

In a previous study (Leveneur et al., 2009), by using similar resins (Dowex 50Wx8) but with different sizes, the presence of internal mass transfer was noticed. Indeed, initial internal mass transfer limitation was present in the case of gelular resins with a degree of cross-linking equal to 8%, essentially for pretreated catalysts with larger particles. In order to take into account this effect to determine the kinetic parameters, the following mathematical expressions were derived.

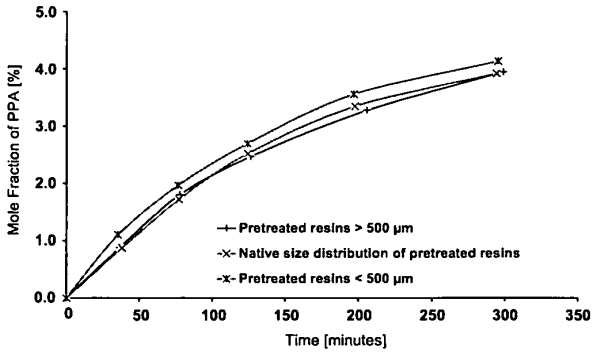



**Fig 7.** The influence of the particle size distribution on the perhydrolysis of propionic acid at 40 °C and with a catalyst loading of 49 g l$^{-1}$.

**Table 4**
Effectiveness factor.

| | $d_p < 500$ μm | Native distribution | $d_p > 500$ μm |
|---|---|---|---|
| $\eta(t = 0\,\text{min})$ | 1.00 | 0.76 | 0.79 |
| $\eta(t = 77\,\text{min})$ | 1.00 | 1.00 | 0.98 |
| $\eta(t = 195\,\text{min})$ | 1.00 | 0.96 | 0.97 |

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### 6.2. Mathematical model of the batch reactor

The methodology to take into account the mass transfer phenomena on the kinetics is similar to the one developed by Silva and Rodrigues (2006), however, it is applied to a different system and moreover the particle size distribution is considered in the present study. The mathematical treatment of the diffusion phenomenon is divided into two parts: particle model and the batch reactor with the particle size distribution. For the sake of simplicity, the most important derivations will be presented in this chapter. More details can be found in Appendix A.

#### 6.2.1. Catalyst particle model

The particle size distribution is included in the reaction–diffusion model for the porous catalyst particle. Spherical particles with the radius $r_j$ are considered in the sequel. The heterogeneously catalyzed process appears on the acid sites of the solid catalyst, while the homogenously catalyzed reactions take place in the pores of the catalyst.

For an infinitesimal volume element in the particle, the mass balance of a component ($i$) can be written as

$$(N_i A)_{in} + r_i' \Delta m + r_i \Delta V_L = (N_i A)_{out} + \frac{dn_i}{dt} \tag{15}$$

where $r_i'$ is the catalytic reaction rate for the heterogeneous system in mol s$^{-1}$ kg$^{-1}$, $r_i$ is the catalytic reaction rate for the homogeneous part in mol s$^{-1}$ m$^{-3}$, $N_i$ is the flux of a component ($i$) in mol m$^{-2}$ s$^{-1}$.

According to the manufacturer, the porosity $\varepsilon_P$ of Amberlite IR-120 is medium, then the value of 0.5 was applied; and the density of this material is equal to 1.26 kg l$^{-1}$.

After some mathematical treatments, and by considering the spherical shape of the catalyst particles with a radius $r_j$. Eq. (15) becomes:

$$\frac{\partial C_{pi}}{\partial t} = \frac{r_i' \rho_P}{\varepsilon_P} + r_i - \frac{1}{\varepsilon_P r_j}\frac{\partial N_i}{\partial X} - \frac{2}{\varepsilon_P r_j X} N_i \tag{16}$$

$X$ is a dimensionless coordinate equal to $r/r_j$.

To calculate the flux of a component ($N_i$), the law of Fick is used:

$$N_i = -D_{ei}\frac{\partial C_{pi}}{\partial r} = -\frac{D_{ei}}{r_j}\frac{\partial C_{pi}}{\partial X} \tag{17}$$

where $D_{ei}$ is the effective diffusion coefficient.

Eq. (17) is inserted in Eq. (16), leading to

$$\frac{\partial C_{pi}}{\partial t} = \frac{r_i' \rho_P}{\varepsilon_P} + r_i + \frac{D_{ei}}{\varepsilon_P r_j^2}\left(\frac{\partial^2 C_{pi}}{\partial X^2} + \frac{2}{X}\frac{\partial C_{pi}}{\partial X}\right) \tag{18}$$

where $X \in [0,1]$. The following boundary conditions are valid: $C_i(X=1) = C_{pi}$ in bulk phase and $(\partial C_{pi}/\partial X)_{X=0} = 0$ for symmetry reasons.

The effective diffusion coefficient $D_{ei}$ is defined as: $D_{ei} = (\varepsilon_P/\tau_P)D_i$, where $D_i$ is the molecular diffusion coefficient for a component ($i$), and was determined by using Wilke–Chang equation. Eq. (18) is solved numerically for each particle size to obtain the concentration profiles in the particles. The molar volumes of the dissolved components and the liquid viscosity are included in the Wilke–Chang equation. The molar volumes were calculated from the atomic increments of Le Bas.

Typical values of the diffusion coefficient $D_i$ at 45 °C are listed in Table 5.

**Table 5**
Diffusion coefficient values of the different species at 45 °C

| | Molecular diffusion coefficient (m$^2$ s$^{-1}$) |
|---|---|
| PA | $1.82\times10^{-9}$ |
| AA | $2.23\times10^{-9}$ |
| PPA | $1.68\times10^{-9}$ |
| PAA | $1.85\times10^{-9}$ |
| Water | $4.68\times10^{-9}$ |
| Hydrogen peroxide | $4.22\times10^{-9}$ |

#### 6.2.2. Batch reactor model with particle size distribution

A batchwise operating stirred tank reactor is considered. Due to vigorous stirring, external mass transfer is suppressed, and concentration gradients in the bulk phase vanish (Leveneur et al., 2009).

The size distribution of the catalysts particle is accounted for in the modelling. Thus, the balance of a component ($i$) becomes:

$$\sum_j N_{ij} A_j + r_i V_L = \frac{dn_i}{dt} \tag{19}$$

In Eq. (19), $r_i$ is the homogeneous rate due to the dissociation of carboxylic acid, and $A_j$ is the total surface area of particles with radius $r_j$. The total number of particles with radius $r_j$ is $n_{pj}$, thus $A_j = n_{pj} 4\pi r_j^2$. The molar amount ($n_i$) is expressed with concentration and volume, $n_i = C_i V_L$, where $V_L$ is the volume of the reaction mixture and $C_i$ the concentration in the bulk phase. The balance equation is rewritten to

$$\frac{\partial C_i}{\partial t} = r_i + \frac{4\pi}{V_L}\sum_j n_{pj} N_{ij} r_j^2 \tag{20}$$

where $N_{ij}$ is obtained from Eq. (17) at $X = 1$ (outer surface).

The fraction with radius $r_j$ is denoted by $y_j$, i.e., $n_{pj} = y_j n_p$ where $n_p$ is the total number of particles in the reactor. Furthermore, the approximate average radius $\bar{r}$ is introduced as follows $\bar{r} = \sqrt{\sum_j y_j r_j^2}$, the ratio to $A_p/V_L$ is denoted by $a_p$ and $r_j/\bar{r} = x_j$.

The final expression equals of the mass balance equation is

$$\frac{\partial C_i}{\partial t} = r_i + a_p \sum_j y_j N_{ij} x_j^2 \tag{21}$$

For the case of equal-sized particles $j = 1$, $y_j = 1$ and $x_j = 1$ in Eq. (21), a standard model for porous particle (PSD) is obtained. Eq. (21) is valid for a discrete particle size distribution. From Fig. 1, one can notice that the particle size distribution can be assumed continuous in the range 320–898 μm. However, particles with a diameter lower than 238 μm represents ca. 5% of the distribution; and, furthermore, the internal mass transfer in this diameter range is absent. For that reason in the model, only particles in the range 320–898 μm were taken into account for the diffusion, the PSD can easily be replaced with a corresponding continuous distribution of particle sizes as shown below.

After some mathematical treatments, the mass balance including the continuous PSD becomes:

$$\frac{dC_i}{dt} = r_i + 2a_p \int_0^{r_{max}/\bar{r}} N_i y(x) x \, dx \tag{22}$$

Eqs. (18) and (22) are both coupled in order to estimate the tortuosity factor $\tau$ of the resins and to get the concentration profiles in the particles. The model equations were solved numerically by discretizing the partial differential equations (PDEs) with respect to the spatial co-ordinate ($X$). Central finite difference formulae were used to approximate the first and second derivatives. Thus, the PDEs were transformed to ordinary differential equations (ODEs). The ODEs were solved with the backward difference method. In practice, the discrete form of the particle size distribution was used in numerical simulations, since the integral in Eq. (22) should in any case be solved numerically. Eq. (21) represents *de facto* the discretization of Eq. (22) for the numerical solution.

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## 7. Kinetic modelling and results

### 7.1. Homogenous catalysis

The values of $\Delta H_r^0$ and $K_{ref}^T$ were estimated from separate experiments carried out for a long time until the chemical equilibrium was reached. The parameter $\Delta H_r^0$ stands for the standard reaction change enthalpy of the perhydrolysis reaction, and $K_{ref}^T$ is the true equilibrium constant at a particular temperature. The parameter estimation was carried out by a special software Modest (Haario, 2001). The objective function $\theta$ was minimized by using Simplex and Levenberg–Marquardt algorithms. This objective function was defined as follows $\theta = \sum(y_i - \hat{y}_i)^2$ where $y_i$ is the experimental value and $\hat{y}$ is the estimated value. The concentrations of CA, PCA and $H_2O_2$ were included in the objective function with equal weights. In this section, the results obtained by the kinetic model of the perhydrolysis of acetic acid catalyzed by sulphuric acid will be presented.

#### 7.1.1. Determination of kinetics and thermodynamic parameters close to equilibrium

In this model, four parameters were estimated: $k_{ave}$, $E_a$, $\Delta H_r^0$ and $K_{ref}^T$ with the reference temperature fixed at 30 °C. The temperature dependence of the rate constant was described by a modified Arrhenius equation:

$$k = k_{ave} \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ave}}\right)\right) \quad (23)$$

where $k_{ave} = Ae^{-(E_a/RT_{ave})}$, $T_{ave}$ is the average temperature of the experiments. The goal of this modification is to minimize the correlation between the frequency factor and the activation energy during the parameter estimation.

The parameter $\delta$ (Eq. (1)) was assumed to be temperature independent within the temperature range 30–60 °C and equal to 0.35 (based on our previous experimental observations). Thus the equilibrium constant $K^C$ is calculated from

$$K^C = 0.35 * [H_2SO_4]_0 + K_{ref}^T \exp\left(\frac{-\Delta H_r^0}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (24)$$

**Table 6**
Heat of formation of reactants and products in the liquid state.

| | $\Delta H_f^0$ (kJ/mol) |
|---|---|
| $H_2O$ | −285.8 |
| $H_2O_2$ | −187.8 |
| AA | −484.5 |
| PAA | −390.1 |

where $T_{ref}$ is fixed at 30 °C in Eq. (24). Eq. (24) is a combination of Eqs. (1) and (3).

The coefficient of explanation $R^2$ of the kinetic models is defined as follows:

$$R^2 = 1 - \frac{\sum(y_i - \hat{y}_i)^2}{\sum(y_i - \bar{y}_i)^2} \quad (25)$$

where $y_i$ is the experimental value, $\hat{y}$ is the estimated value and $\bar{y}$ is the mean value of the observations.

The explanation coefficient of this model became 99.41%, which shows a good agreement between the experimental and calculated values.

The kinetic parameters $k_{ave}$ and $E_a$ obtained with this model are estimated to be $1.80\times10^{-3}$ l mol$^{-1}$ s$^{-1}$ and 69.94 kJ mol$^{-1}$. These parameters were used as initial ones for the more detailed kinetic model. Table 7 summarizes the estimated values of parameters and their respective statistical data.

From Table 7 it can be concluded that the estimated relative standard error are low for each parameter, and, therefore the parameters are well defined. The parameters $K_{ref}^T$ and $\Delta H_r^0$ were estimated to be 2.39 and −5.66 kJ/mol. It should be emphasized that the main aim of this model is the achievement of these thermodynamic parameters, while the values of the kinetic parameters are only preliminary ones.

Table 6 summarizes the heat of formation $\Delta H_f^0$ of the different reactants and products during the perhydrolysis of acetic acid; where the values of $\Delta H_f^0$(AA), $\Delta H_f^0(H_2O)$ and $\Delta H_f^0(H_2O_2)$ were obtained from Lide (1995), and $\Delta H_f^0$(PAA) was measured by Havel and Greschner (1966).

By using the value of the heat of formation from Table 6, the standard enthalpy of reaction for the perhydrolysis of acetic acid is equal to −3.62 kJ mol$^{-1}$, which is close to the estimated value. However, from the study of Dul'neva and Moskvin (2005), this value is equal to −13.7 kJ mol$^{-1}$, which is higher than the two previous values. This difference can be explained by the difficulty to establish when the equilibrium is reached and the non-ideality of the solution in the presence of sulphuric acid.

#### 7.1.2. Kinetic model

In this model, only the kinetic parameters were estimated. Eq. (5) was used for the modelling and the modified Arrhenius equation was applied.

Three parameters were estimated in this model: $k_{ave}$, $E_a$ and $\delta$ which is defined as the coefficient in Eq. (1): $K^C = \delta * [H_2SO_4]_0 + K^T$. The explanation coefficient of the model became 99.41%. Table 7 gives the value of the estimated parameters and the statistical data.

The values of $k_{ave}$ and $E_a$ are rather similar to those from the preliminary model. The present model is more accurate for

**Table 7**
Summary of the estimated parameters and statistical data at $T_{ave} = 45$°C for the perhydrolysis of acetic acid (left) and propionic acid (right) for both catalytic systems.

| Parameters | Estimated | Errors (%) | Parameters | Estimated | Errors (%) |
|---|---|---|---|---|---|
| *Equilibrium parameters* | | | *Equilibrium parameters* | | |
| $K^T$ (30 °C) | 2.39 | 3.4 | $K^T$ (30 °C) | 2.05 | 2.4 |
| $\Delta H_r^0$ (kJ mol$^{-1}$) | −5.66 | 25.6 | $\Delta H_r^0$ (kJ mol$^{-1}$) | −4.17 | 26.9 |
| *Perhydrolysis by sulphuric acid* | | | *Perhydrolysis by sulphuric acid* | | |
| $k_{ave}$ (l mol$^{-1}$ s$^{-1}$) | $1.70\times10^{-3}$ | 3.7 | $k_{ave}$ (l mol$^{-1}$ s$^{-1}$) | $2.00\times10^{-3}$ | 3.3 |
| $E_a$ (kJ mol$^{-1}$) | 75.58 | 3.3 | $E_a$ (kJ mol$^{-1}$) | 44.24 | 6.9 |
| $\delta$ (l mol$^{-1}$) | 0.40 | 33.2 | $\delta$ (l mol$^{-1}$) | 1.33 | 4.8 |
| *Perhydrolysis by Amberlite IR-120* | | | *Perhydrolysis by Amberlite IR-120* | | |
| $k_{ave}$ (l mol$^{-1}$ s$^{-1}$) | $0.99\times10^{-3}$ | 12.7 | $k_{ave}$ (l mol$^{-1}$ s$^{-1}$) | $0.91\times10^{-3}$ | 26.2 |
| $E_a$ (kJ mol$^{-1}$) | 42.5 | 7.0 | $E_a$ (kJ mol$^{-1}$) | 51.4 | 4.6 |
| $K$(AA) (l mol$^{-1}$) | 0.89 | 49.1 | $K$(PA) (l mol$^{-1}$) | 1.39 | 80.5 |

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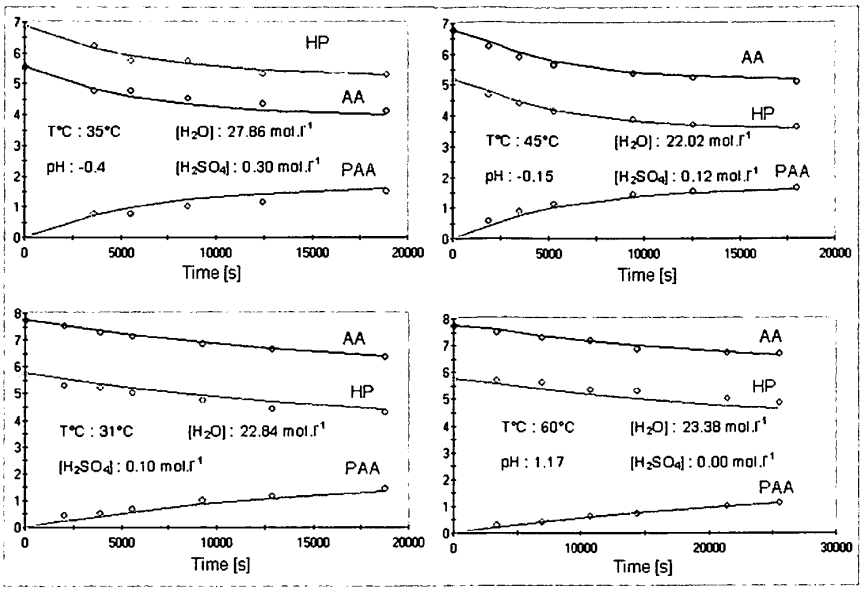



**Fig 8.** Fit of the model to the experiments for the perhydrolysis of acetic acid catalyzed by sulphuric acid.

describing the kinetics, because there are more experiments with different variations included. In this model the experiments were carried out on a shorter reaction time (3–6 h). Examples of the modelling results are illustrated by Fig. 8.

Fig. 8 confirms in an unequivocal manner that the kinetic model fits correctly the experimental data.

### 7.2. Heterogeneous catalysis

Two analogous kinetic models were developed: one for the perhydrolysis of acetic acid and the other one for the perhydrolysis of propionic acid. The estimated equilibrium parameters such as $\Delta H_r^0$ and $K_{ref}^T$ from the homogeneous model were used here, since they are of global character. However, to take into account the slight deviation from the ideality, the concentration-based equilibrium constant $K^C$ was calculated from

$$K^C = \frac{K^T}{K^\gamma} \tag{26}$$

where $K^\gamma$ is the parameter including the activity coefficients. As noticed in Section 4.2, this constant was not estimated in the model but used from the experimental data by assuming that its value is constant over the temperature 30–60 °C.

In these models, three parameters are estimated: $k_{ave}$, $E_a$ and $K$(CA). Preliminary results from the modelling have shown that a value of 2.2 for the tortuosity factor $\tau_P$ gave better statistical results. Due to the complexity to estimate this parameter with a significant statistical reliability, the value of 2.2 was used in this model.

Eq. (14) was used to determine the kinetic and adsorption parameters; the value of $k_{hom}$ (which is a combination of $k_{ave}$ and $E_a$ according to Eq. (23)) was determined by the homogeneous model.

The correlation matrix of the estimated parameters is shown on Fig. 9. From Fig. 9, one can notice that the correlations between the estimated parameters are low, indicating that the parameters are well identified.

| | k | Ea | K(AA) |
|---|---|---|---|
| k | 1 | | |
| Ea | 0.40 | 1 | |
| K(AA) | 0.97 | 0.25 | 1 |

| | k | Ea | K(PA) |
|---|---|---|---|
| k | 1 | | |
| Ea | 0.01 | 1 | |
| K(PA) | 0.99 | -0.03 | 1 |

**Fig 9.** Correlation matrix for the kinetic model.

The explanation coefficients of both models became higher than 99%. Table 7 gives the values of the estimated parameters and the statistical data.

The value of the adsorption coefficient for water on the resin $K_7^C$ at 45 °C is equal to 0.72 by using Altiokka (2007) equation. The standard errors of the kinetic parameters, such as $k_{ave}$ and $E_a$, are relatively low in both reaction systems. However, the standard error for the adsorption coefficient of the carboxylic acids is relatively high probably due to the fact that in the modelling it was assumed to be temperature independent.

Some modelling results are displayed in Figs. 10 and 11.

Figs. 10 and 11 confirm that the model fits correctly the experimental data in case of the perhydrolysis of acetic and propionic acid catalyzed by Amberlite IR-120.

Figs. 12 and 13 represent the concentration profile of peroxyacetic acid versus time and radius location in case of a particle with a diameter equal to 898 μm at 30 and 60 °C, respectively.

Figs. 12 and 13 were obtained by simulating the kinetic-diffusion data for an experiment of acetic acid perhydrolysis carried out at 30 and 60 °C, the catalyst loading of 57.42 g $l^{-1}$ and equimolar concentrations of reactant. The concentration at the bulk is located at 449 μm and concentration in the centre of the particle is located at 0 μm.

One can notice the presence of an internal mass transfer limitation at 30 and 60 °C, Fig. 12 shows that the concentration of PAA increases from 0 to 2.43 mol $l^{-1}$ when moving from the outer surface to the centre of the particle. The internal diffusion is essentially present at the beginning of the reaction, while, the concentration of PAA is uniform throughout the whole particle after 100 min at 60 °C. As the reaction proceeds, the rate becomes slower, and the effect of diffusion is diminished.

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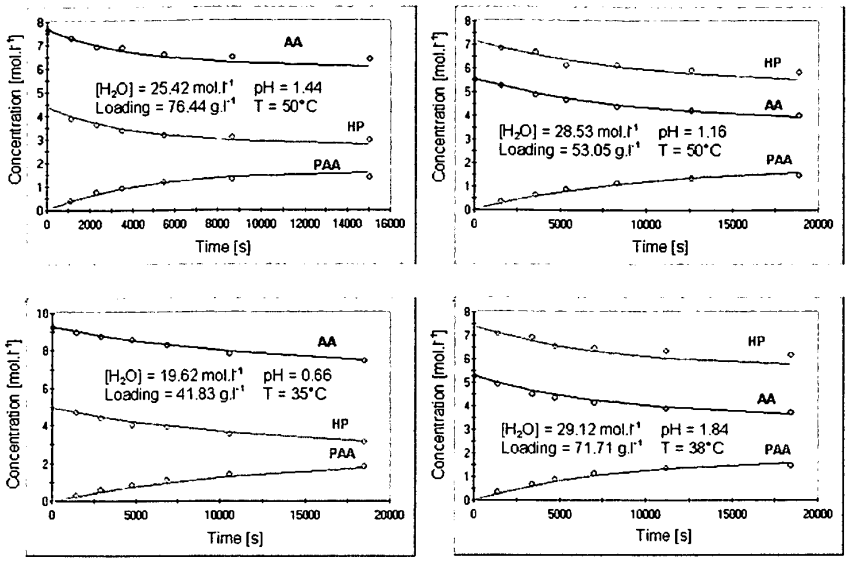



**Fig 10.** Fit of the model to the experiments for the perhydrolysis of acetic acid catalyzed by Amberlite IR-120.

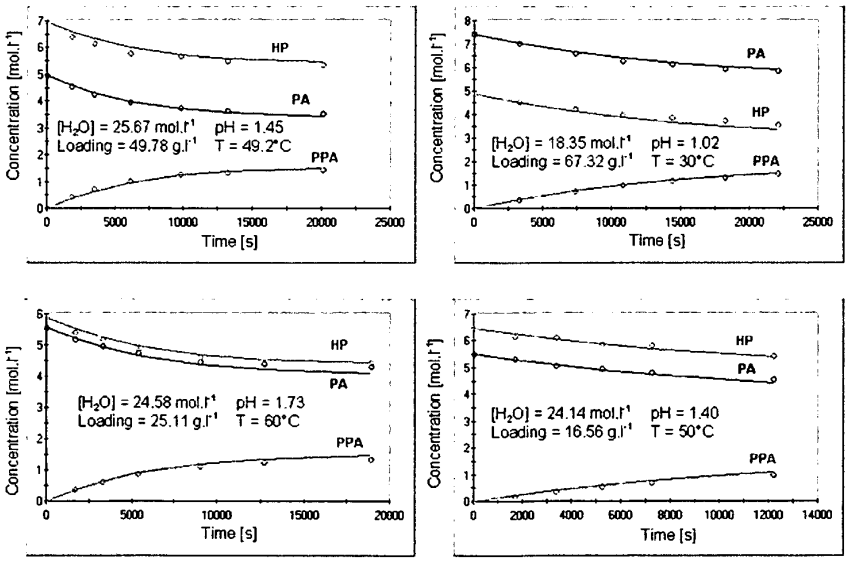



**Fig 11.** Fit of the model to the experiments for the perhydrolysis of propionic acid catalyzed by Amberlite IR-120.

### 7.3. Comparison of two catalytic systems

Table 7 summarizes the kinetic, equilibrium, and mass transfer parameters obtained in case of the perhydrolysis of acetic and propionic acid catalyzed by the homogeneous catalyst, sulphuric acid and the heterogeneous catalyst, Amberlite IR-120.

Table 7 reveals that the standard errors for the estimation of the equilibrium parameters are low. The absolute value of the enthalpy of reaction and equilibrium constant are higher in case of experiments carried out with acetic acid, which imply that the energy amount released by this reaction is higher.

The standard errors for the parameters in perhydrolysis of carboxylic acids with sulphuric acid are low, which confirm the validity of the estimation. The higher energy of activation in case of the perhydrolysis of acetic acid reaction implies that to reach the transition state, more energy is required than for propionic acid. However, the rates of formation of peroxyacetic and peroxypropionic acids are similar. The value of the parameter $\delta$, which describes the

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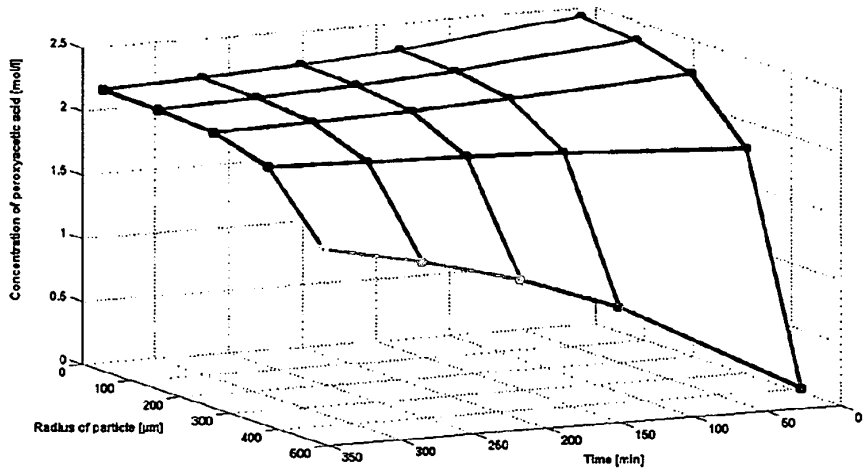



**Fig 12.** Concentration profile for peroxyacetic acid inside a particle of 898 µm at 30 °C.

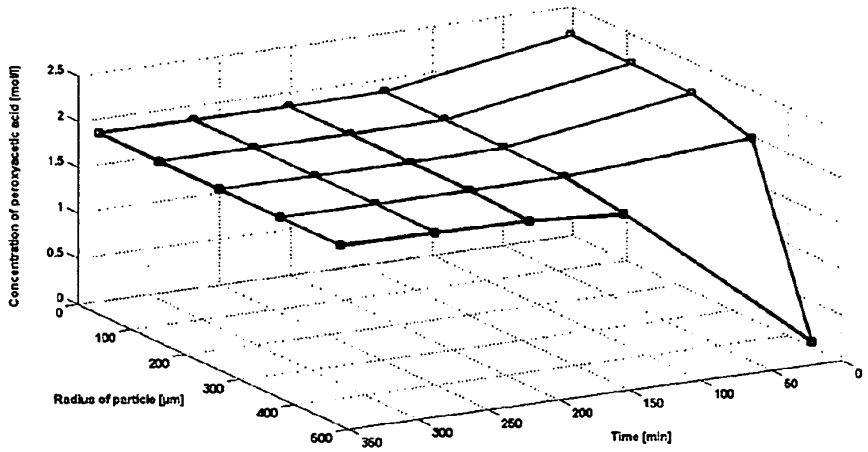



**Fig 13.** Concentration profile for peroxyacetic acid inside a particle of 898 µm at 60 °C.

non-ideality of the solution, in the case of experiments carried out with acetic acid is lower than propionic acid. This means that the non-ideality due to sulphuric acid is lower for peroxyacetic than for peroxypropionic acid solution.

In case of perhydrolysis by Amberlite IR-120, the estimated kinetic parameters are similar for acetic and propionic acid, with low values of the standard errors. Based on the model, a value of 2.2 for the tortuosity factor gives better statistical response.

By comparing the kinetics parameters for the perhydrolysis of carboxylic acid catalyzed by sulphuric acid and by Amberlite IR-120, one can notice that these values are on the same order of magnitude. Obviously, the presence of internal mass transfer limitations in the beginning of the reaction slows down the heterogeneous system. However, this effect should be taken into account when real intrinsic kinetics is pursued, and also in the development of a continuous process since large particles are typically preferred in a continuous fixed bed to suppress the pressure drop.

## 8. Conclusions

A kinetic-diffusion model was developed in batch mode for synthesis of peroxycarboxylic acids (acetic and propionic acid) starting from the corresponding carboxylic acids and hydrogen peroxide using sulphuric acid and pretreated Amberlite IR-120 in a temperature range 30–60 °C. The models were shown to be correct for a water concentration range of 17–40 M, sulphuric acid concentration of 0–1.41 M and for a reactant concentration range of 2–8 M. No decomposition of peroxycarboxylic acids or hydrogen peroxide was noticed.

Pretreatment of resins at different temperature and pressure did not have any influence on the kinetics of the perhydrolysis reaction.

Particle size distribution of the catalyst was determined in water, and it was noticed that the fraction of particles with a diameter higher than 500 µm was increased by ca. 16% compared to dry particles. The swelling effect can be concluded to be negligible. The presence of an internal mass transfer limitation in the beginning of the reaction was noticed by using different particle sizes. This internal mass transfer effect was taken into account in the kinetic model by using the particle size distribution of Amberlite IR-120, and the tortuosity factor was estimated to be 2.2.

Based on the equilibrium analysis, the solution of perhydrolysis of carboxylic acid catalyzed by sulphuric acid was shown to be non-ideal, and this non-ideality was quantified by the factor $\delta$. The standard enthalpy change of reaction $\Delta H_r^0$ of the perhydrolysis of acetic

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acid was estimated to be $-5.66\,kJ\,mol^{-1}$, which is lower than the one for the perhydrolysis of propionic acid reaction, $-4.17\,kJ\,mol^{-1}$, indicating that the synthesis of PAA is slightly more exothermic that the synthesis of PPA.

In case of the experiments carried out with pretreated Amberlite IR-120, a minor deviation from the ideality was noticed, but the amount of catalyst does not influence the chemical equilibrium. Kinetic modelling of carboxylic acids perhydrolysis with sulphuric acid showed that the energy of activation in case of acetic acid ($75.58\,kJ\,mol^{-1}$) is higher than for propionic acid ($44.24\,kJ\,mol^{-1}$).

An Eley–Rideal mechanism was applied, and the protolysis of carboxylic acid was taken into account to derive the kinetic equation for the system influenced by heterogeneous catalyst. The kinetic-diffusion modelling of the perhydrolysis of carboxylic acid by pretreated Amberlite IR-120 shows that the energy of activation in case of acetic acid ($42.5\,kJ\,mol^{-1}$) is similar to that of propionic acid ($51.4\,kJ\,mol^{-1}$). The adsorption coefficients of the carboxylic and peroxyarboxylic acid were supposed to be equal, due to their similar structures, and they were estimated to be in the range of $0.90–1.40\,l\,mol^{-1}$.

The values of kinetic parameters ($k_{ave}$ and $E_a$) for sulphuric acid and pretreated Amberlite IR-120 catalyst are close (see Table 7). Thus, production of these peroxycarboxylic acids via heterogeneous catalysis is feasible, and could avoid the drawbacks associated with the use of sulphuric acid. Kinetic modelling for the synthesis of PPA and PAA shows that the estimated parameters were similar in both cases. The kinetic model and the diffusion model can be used for the design of batch reactors, and they can be easily extended to continuous fixed bed reactors.

## Notation

| | |
|---|---|
| $a_p$ | interfacial area-to-liquid volume, $m^{-1}$ |
| $D_{ei}$ | effective diffusion coefficient, $m^2\,s^{-1}$ |
| $D_i$ | molecular diffusion coefficient, $m^2\,s^{-1}$ |
| $E_a$ | activation energy, $kJ\,mol^{-1}$ |
| $\Delta H_f^0$ | heat of formation of specie, $kJ\,mol^{-1}$ |
| $\Delta H_r^0$ | standard enthalpy change of reaction, $kJ\,mol^{-1}$ |
| $k$ | rate constant, $l\,mol^{-1}\,s^{-1}$ |
| $K$ | adsorption coefficient, $l\,mol^{-1}$ |
| $K^C$ | equilibrium constant, based on concentrations |
| $K^T$ | true thermodynamic constant, based on activities |
| $K^\gamma$ | equilibrium constant, based on coefficients of activity |
| $n$ | amount of substance, mol |
| $n_{pj}$ | number of particle with radius $r_j$ |
| $N$ | flux, $mol\,m^{-2}\,s^{-1}$ |
| $Q$ | reaction quotient |
| $r$ | catalyst particle radius, radial coordinate |
| $\bar{r}$ | average radius |
| $r_i$ | generation rate |
| $r_j$ | particle radius |
| $R$ | gas constant, $J\,K^{-1}\,mol^{-1}$ |
| $R^2$ | coefficient of explanation, % |
| $T$ | temperature, K |
| $V$ | volume |
| $X$ | dimensionless coordinate |
| $y$ | frequency function for particle size distribution |

*Greek letters*

| | |
|---|---|
| $\delta$ | parameter which takes into account the non-ideality of the solution |
| $\varepsilon_P$ | porosity of particle |
| $\eta$ | effectiveness factor |
| $\theta$ | objective function |
| $\rho_P$ | density of particle |
| $\tau_P$ | tortuosity of particle |

*Subscripts*

| | |
|---|---|
| ave | average |
| eq | equilibrium |
| het | heterogeneous catalytic system |
| hom | homogeneous catalytic system |
| $i$ | component $i$ |
| $j$ | particle size fraction |
| ref | reference state |
| 0 | initial |

*Abbreviations*

| | |
|---|---|
| AA | acetic acid |
| CA | carboxylic acid |
| PA | propionic acid |
| PAA | peroxyacetic acid |
| PCA | peroxycarboxylic acid |
| PPA | peroxypropionic acid |
| PSD | particle size distribution |

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## Appendix A

### A.1. Catalyst particle model

For an infinitesimal volume element in the particle, the mass balance of a component ($i$) can be written as

$$(N_iA)_{in} + r_i'\Delta m + r_i\Delta V_L = (N_iA)_{out} + \frac{dn_i}{dt} \tag{A.1}$$

where, $r_i'$ is the catalytic reaction rate for the heterogeneous system in $mol\,s^{-1}\,kg^{-1}$, $r_i$ is the catalytic reaction rate for the homogeneous part in $mol\,s^{-1}\,m^{-3}$, $N_i$ is the flux of a component ($i$) in $mol\,m^{-2}\,s^{-1}$.

The relation $\Delta m$, $\Delta V_L$ and $n_i$ can be expressed as $\Delta m = \rho_P\Delta V$ in kg, $\Delta V_L = \varepsilon_P\Delta V$ in $m^3$, $n_i = c_{pi}\Delta V_L = c_{pi}\varepsilon_P\Delta V$ in mol.

By including these relations in Eq. (A.1), the balance is transformed to

$$\frac{\Delta(N_iA)}{\Delta V} + \varepsilon_P\frac{dC_{pi}}{dt} = r_i'\rho_P + r_i\varepsilon_P \tag{A.2}$$

For a spherical particle with radial coordinate ($r$), the area ($A$), the volume ($V$) and the volume element ($\Delta V$) are: $A = 4\pi r^2$, $V = 4/3\pi r^3$ and $\Delta V = 4\pi r^2\Delta r$. The derivative becomes:

$$\frac{\Delta(N_iA)}{\Delta V} = \frac{\Delta(N_i4\pi r^2)}{4\pi r^2\Delta r}$$

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and by letting $\Delta r \to 0$, we get

$$\frac{\Delta(N_i A)}{\Delta V} = \frac{dN_i}{dr} + \frac{2}{r}N_i$$

After introducing the dimensionless coordinate $X = r/r_j$, where $r_j$ is the particle radius, and letting $\Delta V \to 0$, the differential Eq. (A.2) becomes:

$$\frac{\partial C_{pi}}{\partial t} = \frac{r_i' \rho_P}{\varepsilon_P} + r_i - \frac{1}{\varepsilon_P r_j}\frac{\partial N_i}{\partial X} - \frac{2}{\varepsilon_P r_j X}N_i \quad (A.3)$$

To calculate the flux of a component ($N_i$), the law of Fick is used:

$$N_i = -D_{ei}\frac{\partial C_{pi}}{\partial r} = -\frac{D_{ei}}{r_j}\frac{\partial C_{pi}}{\partial X} \quad (A.4)$$

where $D_{ei}$ is the effective diffusion coefficient.

Eq. (A.4) is inserted in Eq. (A.3), leading to

$$\frac{\partial C_{pi}}{\partial t} = \frac{r_i' \rho_P}{\varepsilon_P} + r_i + \frac{D_{ei}}{\varepsilon_P r_j^2}\left(\frac{\partial^2 C_{pi}}{\partial X^2} + \frac{2}{X}\frac{\partial C_{pi}}{\partial X}\right) \quad (A.5)$$

where $X \in [0, 1]$. The following boundary conditions are valid: $C_i(X = 1) = C_{pi}$ in bulk phase and $(\partial C_{pi}/\partial t)_{X=0} = 0$ for symmetry reasons.

The effective diffusion coefficient $D_{ei}$ is defined as: $D_{ei} = (\varepsilon_P/\tau_P)D_i$, where $D_i$ is the molecular diffusion coefficient for a component ($i$), and was determined by using Wilke–Chang equation.

### A.2. Batch reactor with PSD

A batchwise operating stirred tank reactor is considered and the external mass transfer is neglected.

The size distribution of the catalysts particle is accounted for in the modelling. Thus, the balance of a component ($i$) becomes:

$$\sum_j N_{ij}A_j + r_i V_L = \frac{dn_i}{dt} \quad (A.6)$$

In Eq. (A.6), $r_i$ is the homogeneous rate due to the dissociation of carboxylic acid, and $A_j$ is the total surface area of particles with radius $r_j$. The total number of particles with radius $r_j$ is $n_{pj}$, thus $A_j = n_{pj}4\pi r_j^2$. The molar amount ($n_i$) is expressed with concentration and volume, $n_i = C_i V_L$, where $V_L$ is the volume of the reaction mixture. The balance equation is rewritten to

$$\frac{\partial C_i}{\partial t} = r_i + \frac{4\pi}{V_L}\sum_j n_{pj}N_{ij}r_j^2 \quad (A.7)$$

where $N_{ij}$ is obtained from Eq. (A.4) at $X = 1$ (outer surface).

The second term on the right-hand side in Eq. (A.7) requires further consideration. The fraction with radius $r_j$ is denoted by $y_j$, i.e., $n_{pj} = y_j n_p$ where $n_p$ is the total number of particles in the reactor. Furthermore, the approximate average radius $\bar{r}$ is introduced as follows:

$$A_p = n_p 4\pi\bar{r}^2 = \sum_j n_p y_j 4\pi r_j^2$$

gives $\bar{r} = \sqrt{\sum_j y_j r_j^2}$.

The balance Eq. (A.7) can be now rewritten to

$$\frac{\partial C_i}{\partial t} = r_i + \frac{4\pi\bar{r}^2 n_p}{V_L}\sum_j y_j N_{ij}\left(\frac{r_j}{\bar{r}}\right)^2 \quad (A.8)$$

The ratio $n_p 4\pi\bar{r}^2/V_L$ equals to $A_p/V_L$ which is denoted by $a_p$ and $r_j/\bar{r} = x_j$.

The final expression equals of the mass balance equation is

$$\frac{\partial C_i}{\partial t} = r_i + a_p\sum_j y_j N_{ij}x_j^2 \quad (A.9)$$

For the case of equal-sized particles $j = 1$, $y_j = 1$ and $x_j = 1$ in Eq. (A.9) and a standard model for porous particle (PSD) is obtained. Eq. (A.9) is valid for a discrete particle size distribution.

The frequency function $y(x)$ is introduced and one gets $\sum_j y_j N_{ij} z_j$, where $z_j = x_j^2$. By assuming the PSD continuous, then, $y_j z_j$ can be diminished to $\Delta(y_j z_j)$, an infinitesimal fraction.

The term $\sum_j y_j N_{ij} x_j^2$ of Eq. (A.9) becomes $\sum_j N_{ij}\Delta(y_j z_j)$, which is equivalent to $\int N_i y(x')\,dz$, where $z = x^2$ and $dz = 2x'\,dx'$.

Thus, $\sum_j N_{ij} y_j x_j^2$ approaches to $2\int N_i y(x) x'\,dx'$ as the continuous particle size distribution is approached. The mass balance including the continuous PSD becomes

$$\frac{dC_i}{dt} = r_i + 2a_p\int_0^{r_{max}/\bar{r}} N_i y(x)\,dx \quad (A.10)$$

The flux ($N_i$) at the outer of the surface is obtained from the solution of the particle model, according to Eq. (A.4), giving

$$N_i = -\frac{D_{ei}}{r_j}\left(\frac{dC_i}{dX}\right)_{X=1}$$

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# Rates of formation of peroxyacetic acid from hydrogen peroxide and acetic acid in the presence of metal(IV) phosphates

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**Abstract**

Amorphous zirconium, tin, titanium, vanadyl, cerium and scandium/zirconium phosphates have been evaluated in relation to their effects on the catalysed formation of peroxyacetic acid (PAA) from hydrogen peroxide and acetic acid. The rate of formation of PAA remained almost the same whether the phosphates were present or absent, for most of the phosphates. However, by exchanging the acidic hydroxyl centres in ZrPA with scandium(III), it was found that the resulting solid, ScZrPA, strongly accelerated the formation of PAA, even more so than the scandium(III) ions in homogeneous solution. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Tetravalent metal phosphates; Scandium; Peroxyacetic acid; Hydrogen peroxide

## 1. Introduction

The synthesis and application of porous materials has shown extraordinary growth over the past 25 years. The success of these materials as shape-selective catalysts, adsorbents, molecular sieves, sensor materials and ion-exchangers have contributed significantly to advances in basic and applied research. An ultimate important goal in the syntheses of these compounds is control of size, shape and hydrophilic or hydrophobic character of micropores and greater thermal stability so as to control a variety of industrial processes [1–7].

Oxidation of phenol is one important reaction industrially, since it can produce hydroquinone and catechol, both of which are important starting materials for production of fine chemicals used in agrochemicals, pharmaceuticals, flavours and aromatic essences. However, most of the methods available for production of hydroquinone and catechol are not selective to one or the other or they give low yields with large amounts of tarry by-products. Metal(IV) phosphates provide one group of meso- and microporous materials, which have shown promise for selectivity in formation of oxidised products from phenol [8]. It was not clear from this last work whether or not the phosphates affected the course of oxidation directly or indirectly through catalysed formation of peroxyacetic acid (PAA).

Metal(IV) phosphates are interesting as potential catalysts because of their lamellar structures and their Brønsted and Lewis acidic sites, which may be used

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for ion exchange with a range of metal cations. Most of the catalytic activity so far reported in the literature for metal(IV) phosphate has been attributed to their acidic nature [9–13], but the selective oxidation reactions [8] provide an example of a different use for them. The present work reports an investigation into the effects of various phosphates on the rate of formation of PAA from acetic acid and hydrogen peroxide, which is itself a major industrial process.

## 2. Experimental

### 2.1. Characterisation of catalysts and reaction products

For metal(IV) phosphates already described in the literature, sufficient X-ray spectroscopic and other data were obtained to confirm their identities. High-pressure liquid chromatography (HPLC) analysis was performed using a Hypersil ODS column (25 cm × 5 μm). Infrared spectra were recorded on a Fourier-transform spectrometer, liquid compounds as films and solids as KBr disks. A diode array spectrometer was used to record ultraviolet/visible (UV/VIS) spectra. Mass spectra were obtained using electron ionisation at 70 eV. Melting points, $^{1}$H-nuclear magnetic resonance (NMR) and solid state $^{31}$P MAS NMR spectra were measured to characterise the materials. For the latter spectra, chemical shifts are quoted in parts per million relative to phosphoric acid, for which the chemical shift is made equal to zero.

### 2.2. Synthesis of metal(IV) phosphates

Amorphous α-zirconium phosphate (ZrPA) [14], tin phosphate (SnPA) [15], titanium phosphate (TiPA) [16], together with crystalline vanadyl phosphate (VOPC) [17], fibrous crystalline cerium phosphate (CePFC) [18] and pellicular zirconium phosphate (ZrPP) [19] were prepared as previously described in the literature. Amorphous scandium ion-exchanged zirconium phosphate (ScZrPA) and amorphous zirconium tungstate phosphate (ZrWPA) (basic form) were prepared as described below.

#### 2.2.1. Amorphous ScZrPA [20]

Scandium(III) triflate (0.5 g, 2.25 mmol) was added to a sample of zirconium phosphate (ZrPA, 0.32 g, 1.44 mmol) in water (10 ml). The resulting suspension was stirred at room temperature for 3 days after which the solid was filtered off under vacuum (water pump), washed with water (3 × 10 ml) and allowed to dry at room temperature for 18 h to give 0.22 g of product. Elemental analysis: found, $ZrO_2$ 12.9; $P_2O_5$ 10.5; Sc 23.9 (Zr:P:Sc ratio = 2:1:5; 5.3 mmol $Sc^{3+}$ per gram of solid).

#### 2.2.2. Amorphous ZrWPA (basic form) [21]

A solution of zirconyl chloride (10.52 g, 32.65 mmol) in water (20.0 ml) was added slowly to a solution of disodium hydrogen phosphate (14.68 g, 82.50 mmol) and sodium tungstate dihydrate (2.67 g, 8.1 mmol) in water (100 ml), at room temperature and with stirring. The initially clear solution, produced a precipitate after 15 min and this suspension was warmed to 80 °C during 4 h with stirring. After cooling the mixture, the precipitate was filtered off and washed with distilled water until pH = 8 of the filtrate. The residual white solid was air-dried at room temperature for 48 h; $\nu_{max}$ ($cm^{-1}$) 3468, 2371 (OH); 1646 (P–O); 1137 (P–O); 985 (P–O). Found: Zr, 21.0%, W, 2.9%, P, 13.4%; 28.5 $m^2$/g.

### 2.3. Oxidation of phenol with $H_2O_2$ in the presence and absence of metal(IV) phosphates

Because of the many potential variables in these systems, the oxidation of phenol was examined by use of the Simplex method [22]. This method uses sequential optimisation of the variables influencing the outcome of a system, such as a chemical reaction. It requires the repeated observation of the system response, selection of new values for the variables in accordance with the Simplex rules, followed by a new observation, in an iterative process repeated until the optimum response is obtained. In our case, the yields of the reaction products as well as the substrate conversion were the criteria used for the application of the Simplex method.

We have performed a series of reactions with α-ZrPA, to determine the optimum reaction conditions. By changing these conditions, we have found that the variables with greater impact on the reaction were the temperature, the reaction time, the concentration of $H_2O_2$ and the amount of $H_2O_2$ oxidant. The Simplex method was then applied to obtain the following optimum conditions for best yields of

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hydroquinone and catechol: temperature (60 °C), time (6 h), concentration of $H_2O_2$ (35%, w/w) and amount of $H_2O_2$ oxidant (2 mol to each mole of phenol). These define the standard conditions, used in all subsequent oxidations with other metal phosphates [8].

### 2.4. Determination of hydrogen peroxide and PAA in mixtures [23]

The total available oxygen content ($H_2O_2$ and $CH_3CO_3H$) was determined by addition of NaI to an aliquot of a solution of the oxidant, followed by titration (*A*) of the released $I_2$ with sodium thiosulphate. The $H_2O_2$ content was determined on another aliquot of the oxidant by titration (*B*) against ceric sulphate (0.1 M), using ferroin as indicator. The difference ($A - B$) gave PAA content.

### 2.5. Rates of reaction of hydrogen peroxide with acetic acid

#### 2.5.1. In the absence of any added catalyst [20]

Hydrogen peroxide (65%, w/w, 0.2 g, 4 mmol) was added dropwise to acetic acid (4.2 g, 70 mmol) and the resulting solution was stirred gently at room temperature for 6 h. Aliquots were taken at regular intervals to determine the concentrations of PAA and hydrogen peroxide. This reaction is weakly self-catalysed.

#### 2.5.2. With added scandium(III) triflate as homogeneous catalyst [20]

Hydrogen peroxide (65%, w/w, 0.26 g, 5 mmol) was added dropwise to a solution of scandium(III) triflate (0.98 g, 2 mmol of $Sc^{3+}$) in acetic acid (4.2 g, 70 mmol). The solution was stirred at room temperature for 6 h. The amounts of PAA and hydrogen peroxide were determined at intervals.

#### 2.5.3. With added amorphous ScZrPA as catalyst [20]

Hydrogen peroxide (65%, w/w, 0.26 g, 5 mmol) was added dropwise to a mixture of ScZrPA (0.02 g; $1.8 \times 10^{-4}$ mmol of $Sc^{3+}$) in acetic acid (4.2 g, 70 mmol) and the whole solution was stirred gently at room temperature for 6 h. Aliquots of the liquid were removed at intervals to determine the contents of PAA and hydrogen peroxide.

### 2.6. Determination of hydrogen peroxide absorbed by amorphous zirconium phosphate [21]

#### 2.6.1. Content of hydrogen peroxide after brief washing

A sample of ZrPA was added to a stirred aqueous solution of hydrogen peroxide (70%, w/w) at room temperature. At suitable intervals, aliquots of solid plus liquid were removed from the mixture, filtered through a sintered glass funnel and then washed briefly for 10 s with distilled water (2 ml) under suction. The still wet solid was added to the titration solution, where it was stirred for 5 min and then titrated with ceric sulphate solution (0.1 M). This gives the content of hydrogen peroxide, except that which had been removed from the surface by the quick wash.

#### 2.6.2. Content of hydrogen peroxide after thorough washing

Aqueous hydrogen peroxide (70%, w/w) was stirred at room temperature with a sample of amorphous zirconium phosphate. At suitable intervals, aliquots of solid plus liquid were removed from the reaction mixture, filtered with suction and then washed very well (for about 1 min) with distilled water (7 ml) to remove hydrogen peroxide residual on the surface or held just inside the pores. The resulting wet solid was added to the titration solution, where it was stirred for 5 min and then titrated against ceric sulphate solution (0.1 M) to determine the content of hydrogen peroxide.

## 3. Results and discussion

The object of earlier work [8] was to study the catalytic activity of several metal(IV) phosphates, for oxidation of phenol with hydrogen peroxide. As the work proceeded, it became apparent that, in solvents such as acetonitrile, methanol or *tert*-butyl alcohol, no significant oxidation of phenol occurred but that, in glacial acetic acid, oxidation gave various products (Table 1). This solvent effect suggested that PAA was likely to be the effective oxidant, rather than $H_2O_2$ itself. However, the marked variations in selectivity towards different oxidation products (Table 1) indicated that the phosphates must be having a shape effect on either the reaction of oxidant (either $H_2O_2$ or PAA) with phenol or on the rate of formation of PAA or both effects

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Table 1
Distribution of products from oxidation of phenol in the presence of different tetravalent metal phosphates[a]

| | Phosphates | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | α-ZrPA[b] (%) | SnPA[c] (%) | CePFC[d] (%) | TiPA[e] (%) | VOPC[f] (%) | ZrPP[g] (%) | ZrWPA[h] basic (%) | No catalyst (%) |
| Yield of hydroquinone based on phenol conversion | 37.3 | 31.0 | 31.0 | 1.4 | – | – | – | 12.1 |
| Yield of catechol based on phenol conversion | 44.0 | 46.8 | 63.7 | 5.5 | – | – | – | 32.4 |
| Yield of *cis,cis*-muconic acid based on phenol conversion | – | – | | – | – | 16.3 | 5.5 | – |
| Yield of *cis,trans*-muconic acid based on phenol conversion | – | – | | – | – | – | 13.8 | – |
| Phenol conversion (w/w) | 20.9 | 17.1 | 16.8 | 29.2 | – | 24.6 | 28.9 | 20.7 |

[a] Reaction conditions were all similar and are described in Section 2. In all cases, acetic acid was used as solvent. Remaining products are non-identified tars. HPLC was used to monitor the reactions. Quantifications were performed by comparison with calibration curves obtained with known amounts of hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid.
[b] Amorphous zirconium phosphate.
[c] Amorphous tin phosphate.
[d] Fibrous crystalline cerium phosphate.
[e] Amorphous titanium phosphate.
[f] Crystalline vanadyl phosphate.
[g] Pellicular zirconium phosphate.
[h] Amorphous zirconium tungstate phosphate.

combined. The heterogeneous lamellar nature of the phosphates suggested that shape selectivity could be involved with or without catalysed formation of PAA.

Sulphuric and of methylsulphonic acids, are used routinely to catalyse the formation of PAA from hydrogen peroxide (1). Without added strong acid, reaction (1) is very slow.

$$CH_3CO_2H + H_2O_2 \overset{H^+}{\rightleftharpoons} CH_3CO_3H + H_2O \quad (1)$$

Since metal(IV) phosphates have various effective acid strengths [25], it was decided to explore the possibility that the phosphates could be influencing the oxidation through an ability to catalyse the rate of formation of PAA. In typical experiments, a mixture of aqueous hydrogen peroxide and glacial acetic acid was maintained at 60 °C over a period of about 6 h. Aliquots of the liquid were removed at regular intervals and the contents of $H_2O_2$ and $CH_3CO_3H$ were determined by titration. Typical results are shown in Fig. 1. It can be seen immediately that, ZrPA, SnPA and CePFC had no significant effect on the rate of formation of PAA, despite their known acidities. In the case of vanadyl phosphate, there was actually no formation of PAA and the hydrogen peroxide was decomposed. With titanium phosphate, the initially formed PAA was itself decomposed by the phosphate so that the total oxidant level rose initially but then fell over time.

When the effect of ZrPA was examined over a further period of 6–24 h, no more PAA was formed and the total oxidant level remained constant (an equilibrium state). Thus, ZrPA neither significantly altered the rate of formation of PAA (no catalytic effect) nor did it have any effect on the position of equilibrium (no thermochemical effect) in reaction (1) through, e.g., trapping and removing PAA from the reaction products [21].

To discover what other role the porous structure of ZrPA might have on reaction (1), the phosphate was stirred with aqueous 70% $H_2O_2$ alone. Over a period of 6 h, samples of ZrPA were removed. These samples were either washed very quickly with cold water, to remove most $H_2O_2$ from the outside of the phosphate particles or were washed well with water, so as to leave only any $H_2O_2$ remaining tightly bound inside the lamellar structure. The results showed clearly that, after brief washing, about 6% $H_2O_2$ remained adsorbed into the ZrPA and, after extended washing, there still remained about 1% [21]. These results suggest that $H_2O_2$ must penetrate right inside the phosphate structure and possibly be held there by hydrogen

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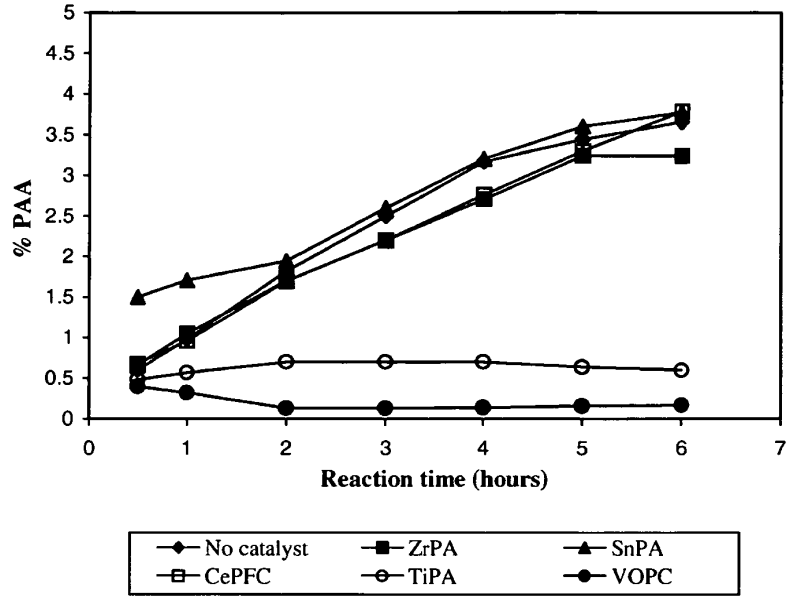



Fig. 1. Formation of PAA from glacial acetic acid and aqueous hydrogen peroxide (35%, w/w) in the absence and presence of metal(IV) phosphates. The percentages of PAA are quoted as millilitres of substrate per 100 ml of solution. The reactions were carried out at 60 °C.

bonding. This indicated that any effect of the phosphates on oxidation of phenol with $H_2O_2$, could occur by affecting selectivity towards product formation in their pores and not by catalysed formation of PAA.

Although previous results show that PAA must be the major phenol oxidant, the effect of the phosphates was not catalytic in formation of the PAA. Since the phosphates did control the type of oxidation product (hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid), it is concluded that they exert shape selectivity [8].

The uncatalysed conversion of acetic acid into PAA with hydrogen peroxide (1) is very slow but can be accelerated with added acid. Good conversions in reasonable reaction time are only possible through the use of very strong acids [24]. Although the metal(IV) phosphates described above contained moderately strong acid centres [8,18,19,25] as determined by titration [26], there were no centres having $pK_a$ between +3.3 and −3.3. Neither the Lewis nor Brønsted acid centres in these metal(IV) phosphates were sufficiently strong as to catalyse PAA formation, more than acetic acid does itself. Use of Sc(III) and La(III) salts as good Lewis acid catalysts in aqueous environments has been reported in the direct acetylation of alcohols [27]. Also, a Nafion-supported scandium catalyst for allylation of carbonyl compounds has been described [28]. Hydrogen peroxide can be considered to be an 'alcohol' and, therefore, it was decided to investigate whether or not scandium compounds would have any effect on the rate of reaction (1). The possibility of homogeneous and heterogeneous catalysis was examined.

When acetic acid was mixed with aqueous hydrogen peroxide at room temperature, in the presence of soluble scandium(III) triflate, formation of PAA was found to be six times faster than when no scandium was present (Fig. 2). Optimum times, temperatures and catalyst concentration for this homogeneous reaction were not investigated. Instead, because a reusable heterogeneous catalyst was preferable to conserve scandium, a sample of ZrPA was stirred with scandium triflate solution to exchange $H^+$ for $Sc^{3+}$. The resulting ScZrPA was used, under the same conditions as for the homogeneous scandium triflate and a greater acceleration in the production of PAA was observed (Fig. 3). If the accelerations are compared on a molar basis for $Sc^{3+}$ content, the heterogeneous catalyst

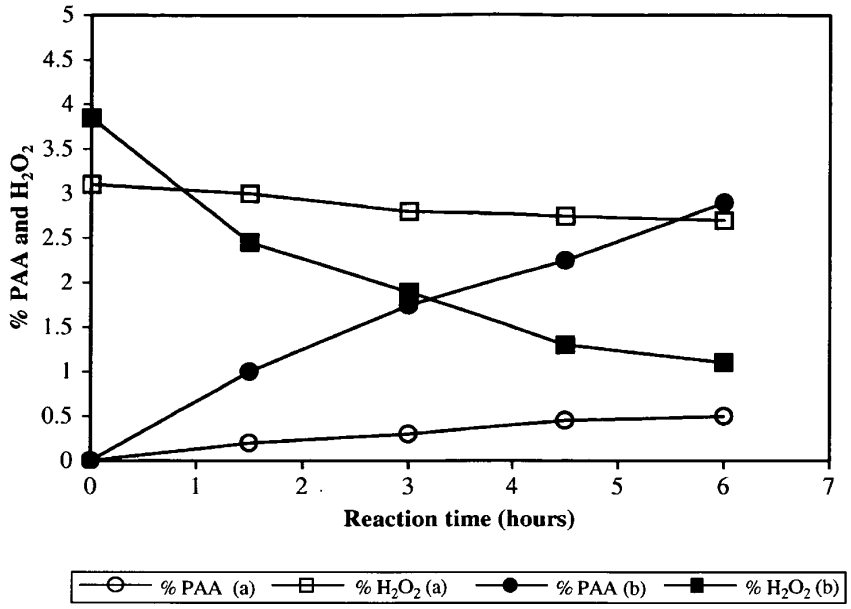



Fig. 2. Formation of PAA and consumption of hydrogen peroxide with: (a) no catalyst and (b) scandium(III) triflate. The percentages of hydrogen peroxide and PAA are quoted as millilitre of substrate per 100 ml of solution. The reactions were carried out at 20 °C.

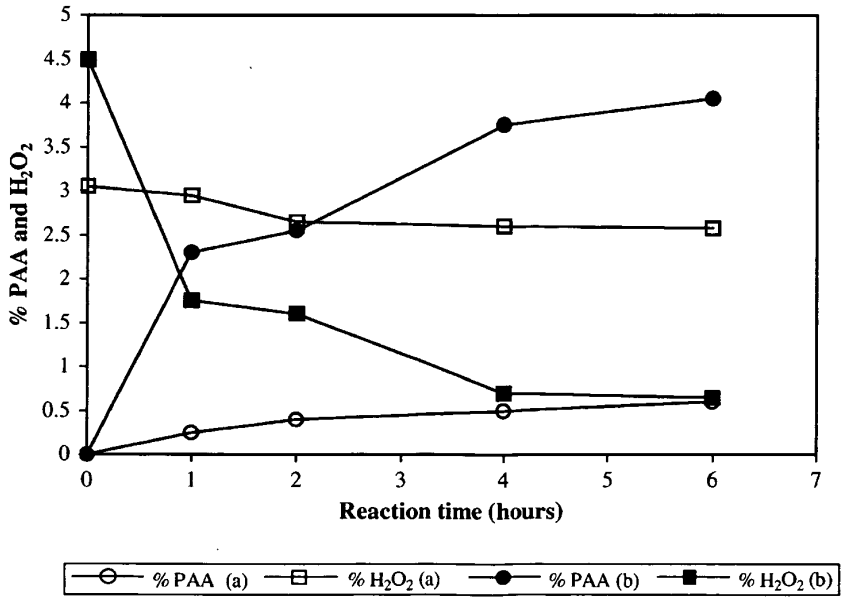



Fig. 3. Formation of PAA and consumption of hydrogen peroxide with: (a) no catalyst and (b) amorphous ScZrPA as catalyst. The percentages of hydrogen peroxide and PAA are quoted as millilitres of substrate per 100 ml of solution. The reactions were carried out at 20 °C.

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was about 20 times more effective than the homogeneous one and some 80 times more effective than the self-catalysed reaction (1).

To clarify the possibility of a homogeneous contribution (Sc release in the media) in the case of the reaction with ScZrPA, we should mention that the latter catalyst was reused for catalysis four times without loss of activity. Additionally, the liquid filtrate from a typical catalysed reaction did not catalyse the formation of PAA unless a fresh amount of the Sc-exchanged phosphate was added. This, together with the greatly enhanced activity of the exchanged material over the homogeneous Sc catalyst, shows clearly that the activity cannot be due to "homogeneous" scandium in solution.

## 4. Conclusions

In the presence of some metal(IV) phosphates, the action of $H_2O_2$ in glacial acetic acid is to produce four major products, viz., hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid. Selectivities and conversions are markedly different depending on the phosphate used, but the overall yields of oxidation products are not greater than those observed for the oxidation of phenol in acetic acid, in the absence of the phosphates. These results indicate that the phosphates have a significant effect on the course of oxidation for the individual oxidation products but do not affect the overall amount of oxidation occurring. The results suggest shape-selectivity towards individual oxidation products.

There was also the possibility that these simple phosphates could influence the oxidation through catalysing the formation of PAA (the true oxidant) inside micro- or mesopores. This effect is unlikely because the rate of formation of PAA from hydrogen peroxide and acetic acid remained almost the same whether the phosphates were present or absent. The lack of catalytic activity towards formation of PAA was unexpected, since the phosphates have well-defined Lewis and Brønsted centres of acidity and the reaction of acetic acid with $H_2O_2$ is strongly catalysed by acid. By exchanging the acidic hydroxyl centres in ZrPA with scandium(III), it was found that the resulting solid ScZrPA strongly accelerated the formation of PAA, even more so than scandium(III) ions in homogeneous solution. Since ZrPA by itself has no effect on the rate of formation of PAA, it cannot be the Brønsted centres that led to the observed acceleration and, instead, it must be Sc-enhanced Lewis acidity that is responsible, viz., ScZrPA is a strong Lewis acid promoter, even under aqueous conditions.

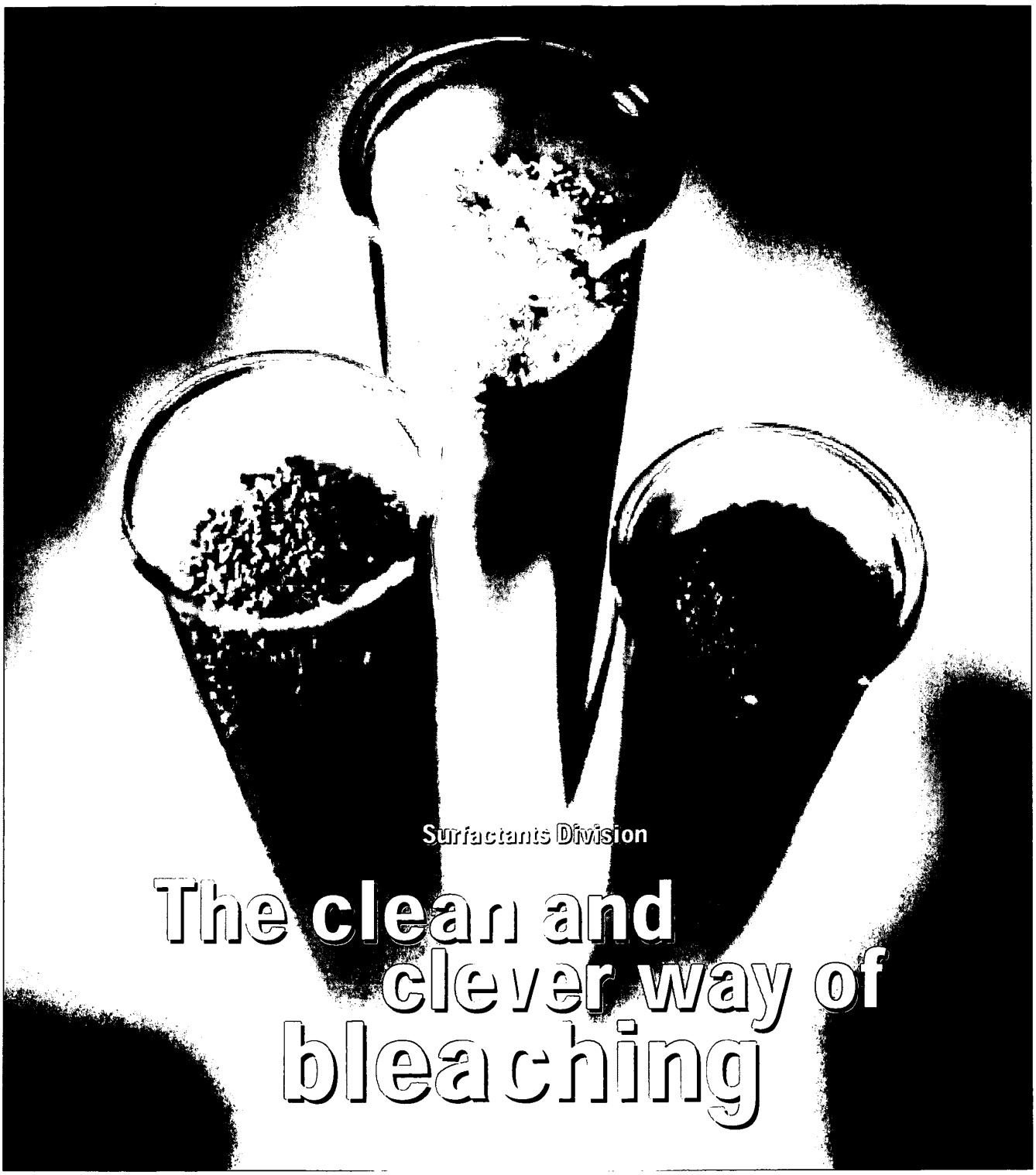
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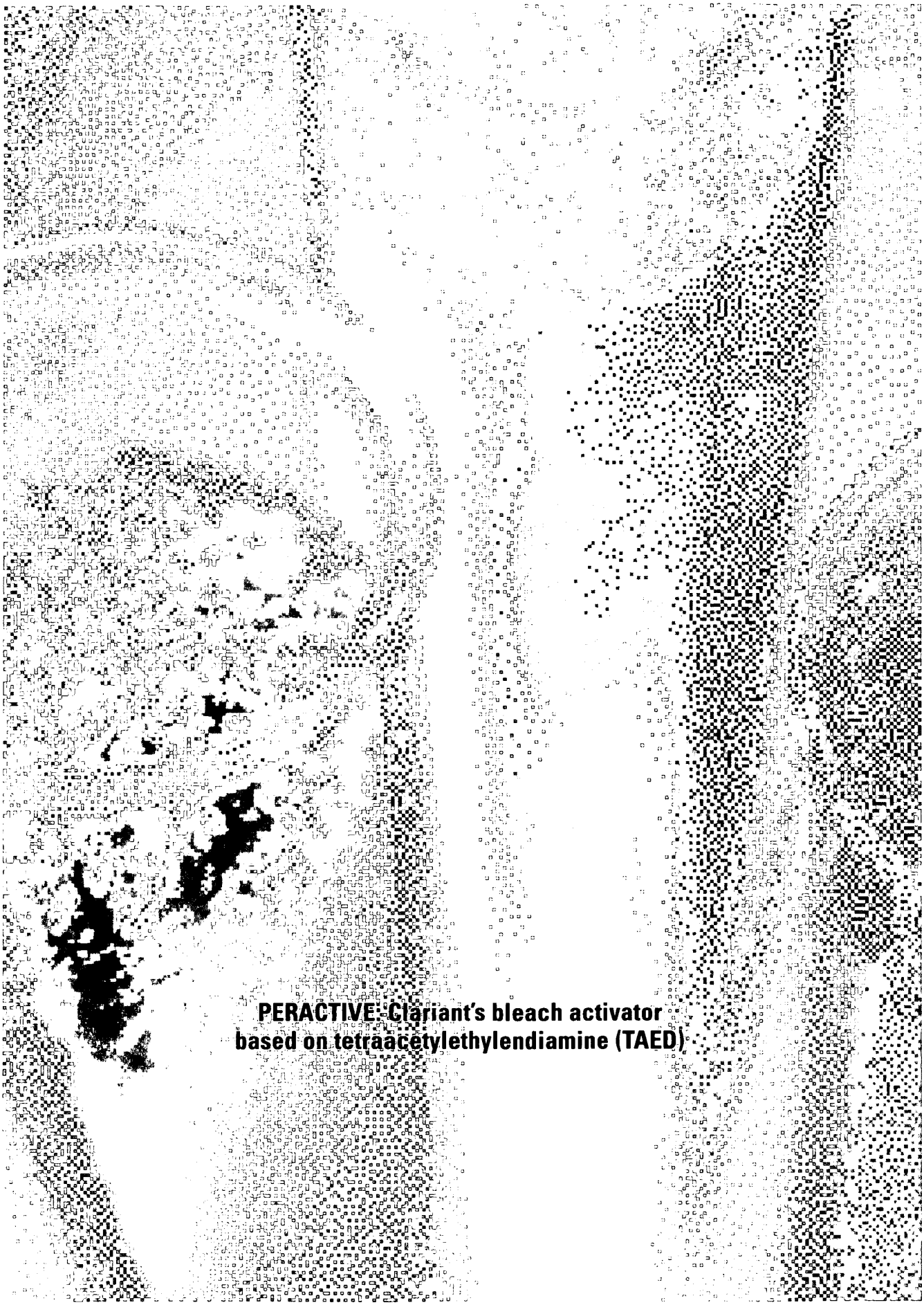
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Exactly your chemistry.

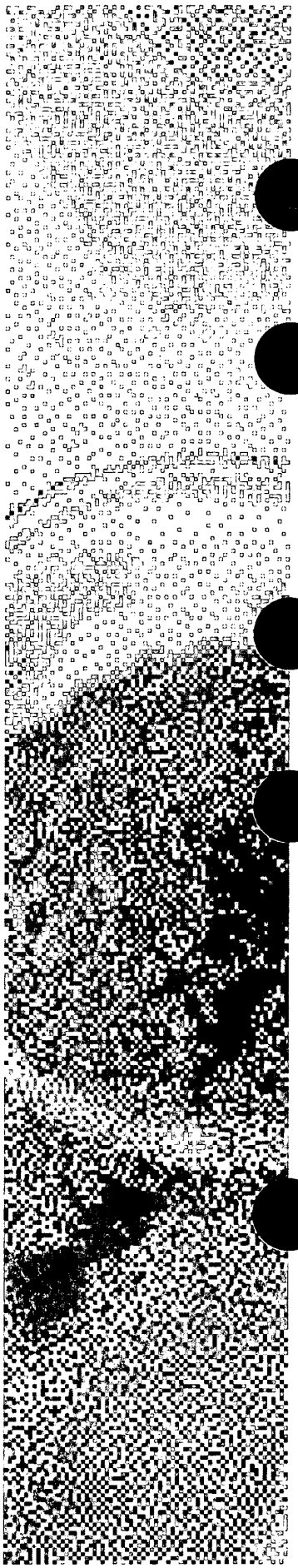
Clariant




® PERACTIVE



**PERACTIVE: Clariant's bleach activator based on tetraacetylethylendiamine (TAED)**



Clariant

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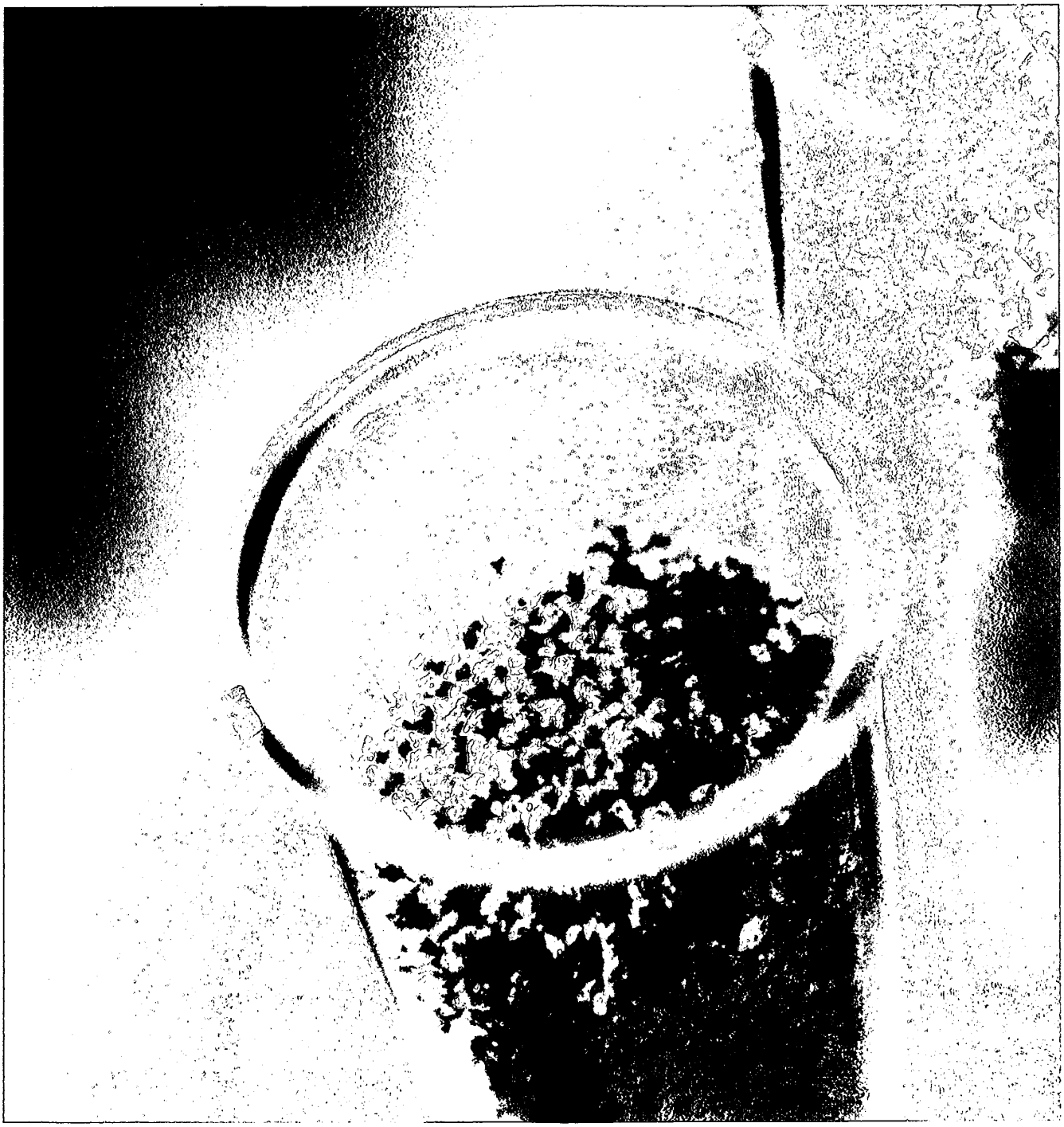
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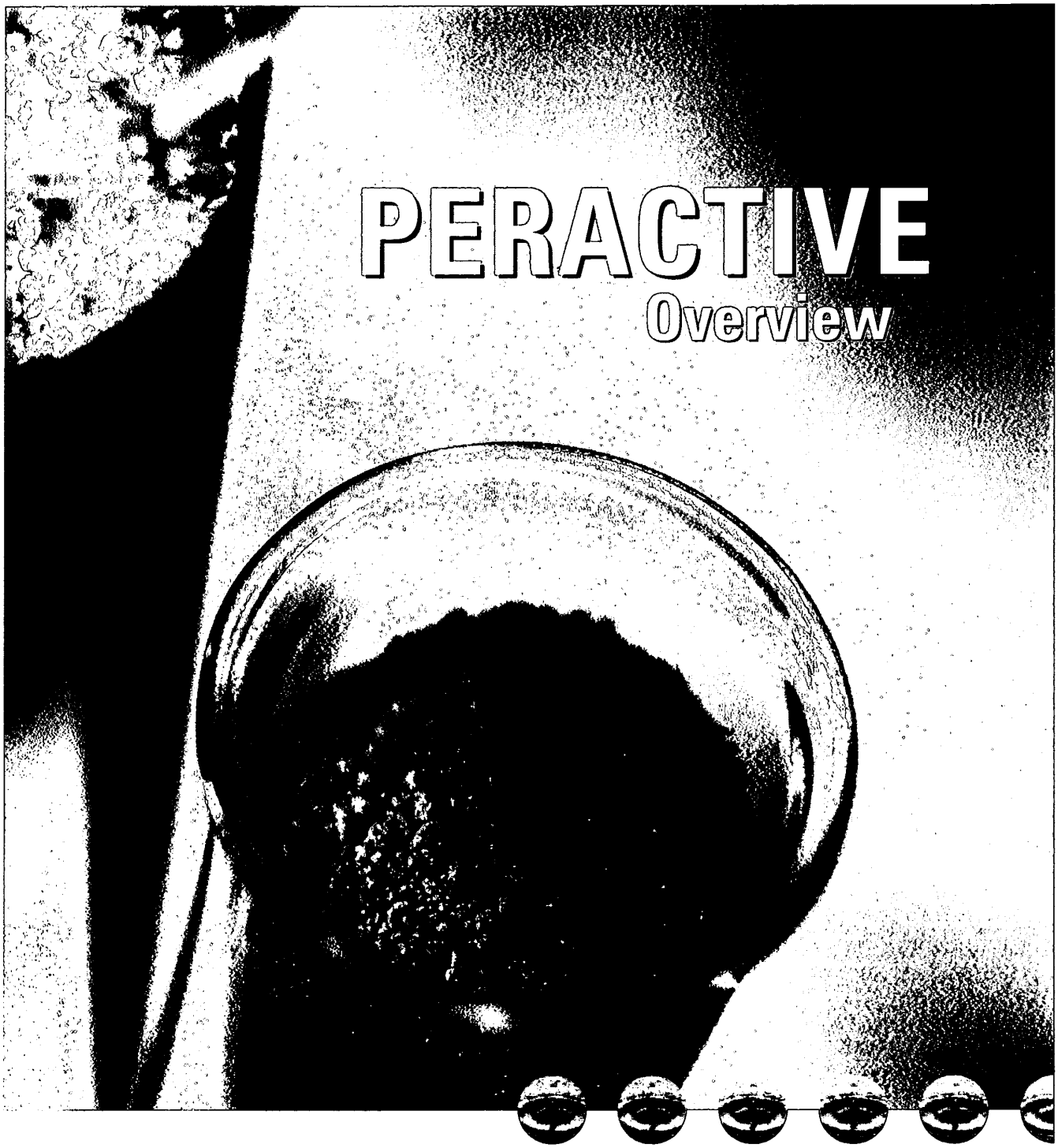
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# PERACTIVE –

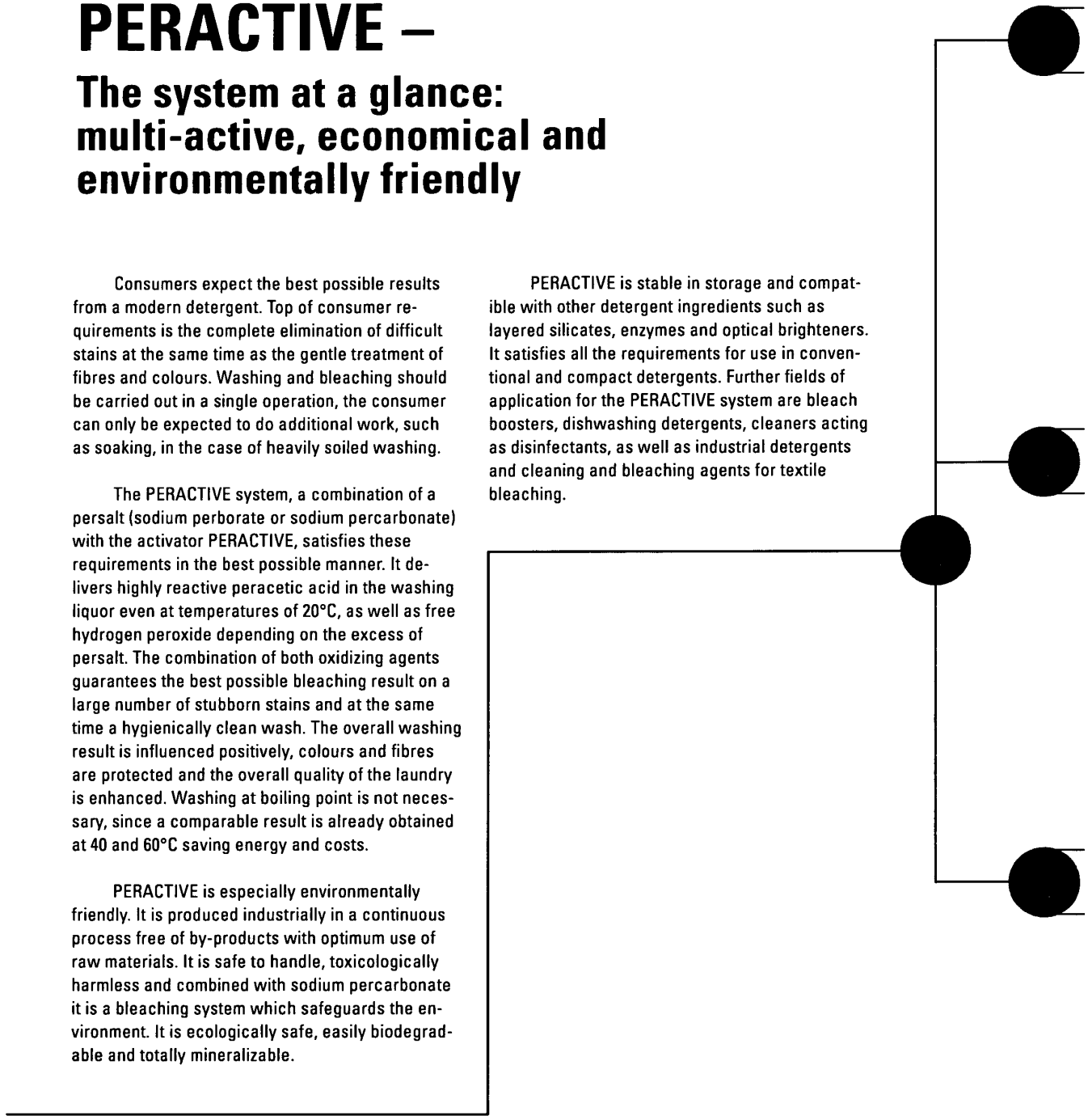
## The system at a glance: multi-active, economical and environmentally friendly

Consumers expect the best possible results from a modern detergent. Top of consumer requirements is the complete elimination of difficult stains at the same time as the gentle treatment of fibres and colours. Washing and bleaching should be carried out in a single operation, the consumer can only be expected to do additional work, such as soaking, in the case of heavily soiled washing.

The PERACTIVE system, a combination of a persalt (sodium perborate or sodium percarbonate) with the activator PERACTIVE, satisfies these requirements in the best possible manner. It delivers highly reactive peracetic acid in the washing liquor even at temperatures of 20°C, as well as free hydrogen peroxide depending on the excess of persalt. The combination of both oxidizing agents guarantees the best possible bleaching result on a large number of stubborn stains and at the same time a hygienically clean wash. The overall washing result is influenced positively, colours and fibres are protected and the overall quality of the laundry is enhanced. Washing at boiling point is not necessary, since a comparable result is already obtained at 40 and 60°C saving energy and costs.

PERACTIVE is especially environmentally friendly. It is produced industrially in a continuous process free of by-products with optimum use of raw materials. It is safe to handle, toxicologically harmless and combined with sodium percarbonate it is a bleaching system which safeguards the environment. It is ecologically safe, easily biodegradable and totally mineralizable.

PERACTIVE is stable in storage and compatible with other detergent ingredients such as layered silicates, enzymes and optical brighteners. It satisfies all the requirements for use in conventional and compact detergents. Further fields of application for the PERACTIVE system are bleach boosters, dishwashing detergents, cleaners acting as disinfectants, as well as industrial detergents and cleaning and bleaching agents for textile bleaching.





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## PERACTIVE – A system with many functions

The PERACTIVE system releases highly reactive peracetic acid in the washing liquor even at room temperature. The peracetic acid reacts with a large number of stains as a result of its oxidation potential. At the same time it acts as a disinfectant and kills bacteria and germs under mild conditions. In addition unpleasant odours (tobacco, cooking smells) are decomposed by oxidation and the efficiency of fragrances is thus enhanced. As a mild oxidizing agent peracetic acid is compatible with most dyes and no damage to the fabric is observed even with frequent use.

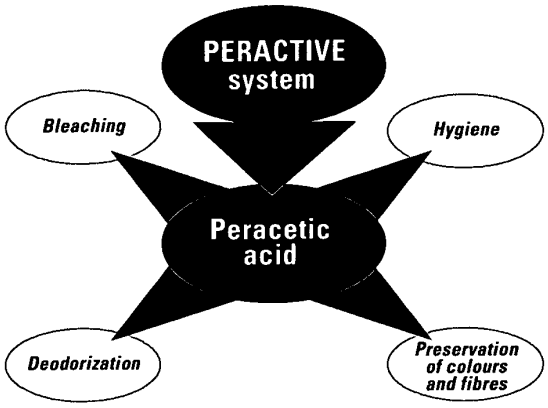



Fig. 1 *Multi-active properties of the PERACTIVE system*

## PERACTIVE – Efficient and economical

The positive effect of PERACTIVE on the bleaching result is visible even at 20°C. It reaches its optimum spectrum of activity in the temperature range of 30 to 60°C. Significantly better stain removal is possible at these temperatures compared to a detergent without PERACTIVE. At temperatures above 70°C excess hydrogen peroxide supports the effect of the peracetic acid. The effective utilization of the activator system is visible if pure peracetic acid is used for bleaching instead of the PERACTIVE system. In this case a comparable result is obtained.

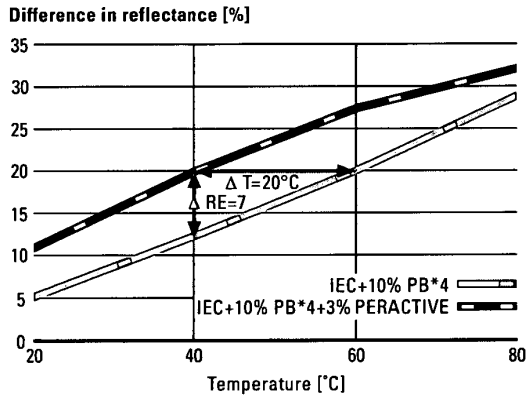



Fig. 2 *Bleaching performance of PERACTIVE/PB compared to PB 30 min. washing time, cotton with tea stains, 1.5 g IEC/l*

## PERACTIVE – Compact and environmentally friendly

The use of PERACTIVE makes it possible to produce effective bleaching systems in terms of weight and volume for incorporation in compact powders. It is possible to reduce the persalt concentration by about 50% without any loss in efficiency. The system proves to be especially environmentally friendly combined with sodium percarbonate, which supplies alkali and at the same time enables additional savings in chemicals to be made.

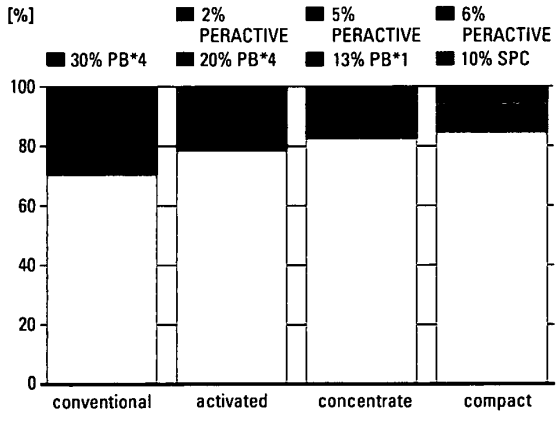


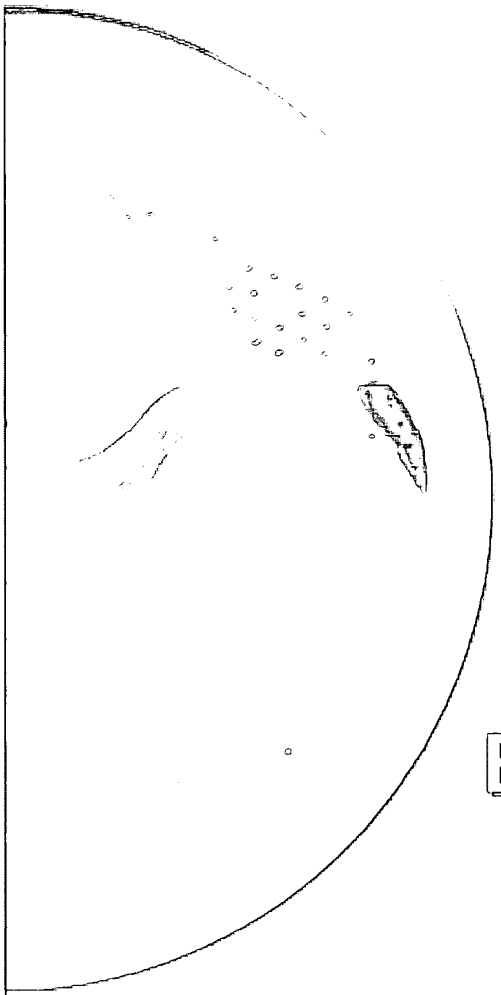

Fig. 3 *Proportion of bleaching systems in heavy duty detergents in Europe 1970–1995*



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# PERACTIVE

## Basics of bleaching

# PERACTIVE –

## The stains and the bleaching agent

Laundry necessarily comes into contact with natural and synthetic dyes in daily use. These may vary in origin: drinks (coffee, tea, fruit juices or red wine), fruit or vegetables (spinach, carrots or marmalade), sauces (ketchup, soya or gravy) or spices (saffron and curry). The natural dyes are often mixtures of substances, whose chemical structures have only been partly explained. Whilst some stains, as long as they have not undergone ageing, can be removed by washing them out quickly, chemical destruction of the chromophore is necessary for stubborn soiling.

Various bleaching agents are used for the washing process worldwide depending on the region. In countries with typical cold wash conditions (10–30°C), such as North America or the Far East, chlorine bleaching (sodium hypochlorite) is still currently used. In 5% solution it is a highly reactive oxidizing agent and disinfectant. However, overdosing of the reactive chemical may easily cause damage to the fibres and dyes in textile fabrics. Furthermore, the formation of halogen-containing substances during storage, use and in the effluent has resulted in search for alternative, more environmentally compatible systems.

Sodium perborate has been used in Europe as a bleaching agent since the beginning of the 20th century. Its crystalline structure guarantees stability in storage and enables it to be incorporated directly in detergents. Unfortunately, the hydrogen peroxide formed on being introduced into water only develops its oxidizing properties at temperatures higher than 80°C, preferably in the pH range of 11 to 12. The effect which can be achieved with persalts alone is only slight at 30–60°C. However, this low temperature range becomes accessible as a result of adding a suitable activator such as PERACTIVE.



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## Bleachable types of stains

Natural dyes can be classified in different groups according to their polarity. Red or reddish brown shades are caused by groups containing phenol, such as occur for example in the anthocyanines (red wine) or flavines (tea). They are ionizable in water and are easily attacked by hydrophilic bleaching agents such as peracetic acid. Water-insoluble, hydrophobic dyes are more difficult to oxidize, such as porphorin systems (chlorophyll in grass) or fully conjugated hydrocarbons (carotenoids).

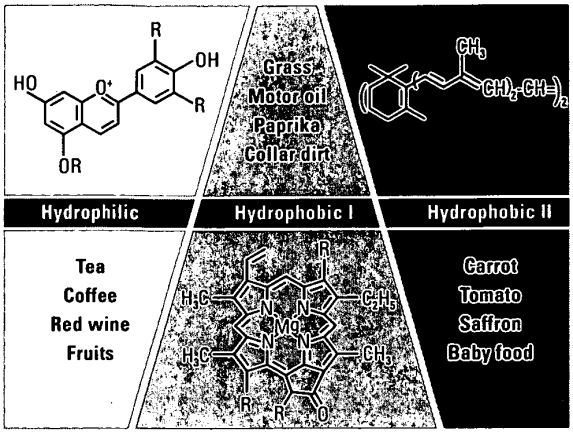



*Fig. 4* *Chemical structures of natural dyes*

## Bleaching systems worldwide

The most aggressive bleaching agent is chlorine bleaching liquor, which is formed on introducing alkali hypochlorites or organic chlorine donators (cyanuric chloride) to water. Hydrogen peroxide is released in the washing liquor from inorganic persalts (sodium perborate) or adducts of the hydrogen peroxide (sodium percarbonate). However, its reactivity is inhibited kinetically and is only realized at temperatures >80°C. Contrary to that in the PERACTIVE system (persalt plus PERACTIVE) a reactive organic peracid is released, which has a bleaching activity at temperatures as low as 30°C.

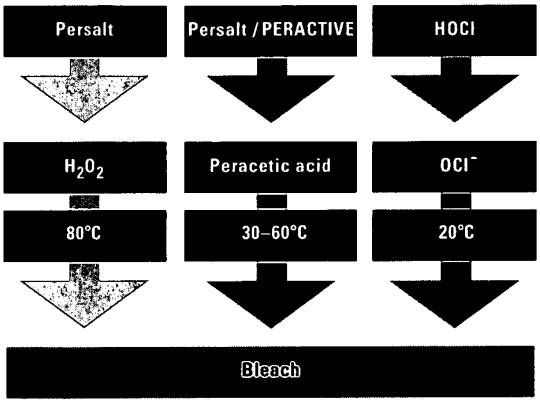



*Fig. 5* *Conventional bleaching systems*

## Factors which influence bleaching

By contrast with the action of surfactants, bleaching is largely independent of the water hardness and the mechanics of the washing process. Good effects are achieved even on soaking.

Whilst the nature and amount of soiling are predetermined, the other factors can be varied over wide limits by the appropriate choice of parameters. From these washing temperature and period are generally specific to the region. Maximum bleaching results can be obtained by the optimum formulation of the bleaching system and the basic detergent.

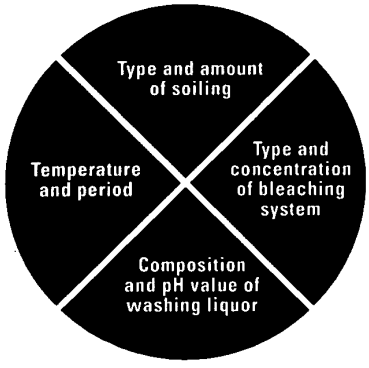



*Fig. 6* *Factors influencing the bleaching process*



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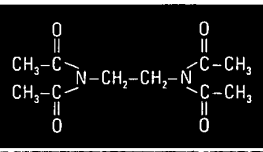
# PERACTIVE –
## Physico-chemical data

PERACTIVE is based on tetraacetylethylenediamine (TAED) which was first described in 1911. Its activity as a bleaching agent activator was recognized at the end of the fifties and it has been a component of modern heavy duty detergents in Europe since the beginning of the eighties. The compound is not protected by patent and can be used in all countries of the world because it is a registered chemical.

The Tetraacetylethylenediamine molecule is electrically neutral, but has a polar character as a result of the two imide structures. In the presence of acceptors it acts as a potential acylating agent with the transfer of two acetyl groups. Its solubility in water is only limited, but increases considerably as the temperature rises. With an intrinsic pH value of 4.5–5.0 it is weakly acidic and is largely stable in water in this pH range. In solution it hydrolyses both in an acid and also in an alkaline medium with the formation of two molecules of acetic acid. It is less soluble in commercial organic solvents. Exceptions are halogenated hydrocarbons such as methylene chloride and chloroform.

By virtue of the process PERACTIVE is obtained in the form of colourless crystals. Its high melting point gives it excellent mechanical and chemical stability, which is further increased for use in alkaline detergents preferably by an additional granulation or coating. PERACTIVE powder and granules are stable almost indefinitely in sealed containers from which heat and moisture are excluded. A faint odour of acetic acid of the PERACTIVE powder is typical of the product, especially after standing for a long time in sealed containers.

It is essential to observe the safety regulations for dustlike products during the technical processing of PERACTIVE powder.

| Structure |  |
|---|---|
| Chemical name | N, N, N', N'-tetraacetylethylenediamine |
| Empirical formula | C 10 H 16 N2 O4 |
| Molecular mass | 228 g/mol |
| CAS no. | 10543 – 57 – 4 |
| EINECS no. | 234 – 123 – 8 |
| MITI no. | 2 – 3577 |
| UIPC nomenclature | N, N'-1,2-ethanediylbis (N-acetyl-)acetamide |
| Other names | N, N'-ethylenebis-diacetamide<br>N, N, N', N'-tetraacetyl-1,2-diaminoethane |

*Names and inventory no.*

*Fig. 7*



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## Physical data of PERACTIVE powder

Characteristics of PERACTIVE are the high degree of purity and the high melting point of the compound, which ensure good processing properties. With a theoretical active oxygen content of 140 mg Oa per gram it produces a much higher yield than comparable products. Minimal traces of adhering free acetic acid – caused in production – are responsible for the pH value and faint odour of the activator.

| | |
|---|---|
| **Active content** | **>98.5%** |
| **Appearance** | **white needles** |
| **Odour** | **faintly acetic** |
| **Molecular weight** | **228 g/mol** |
| **Active oxygen** | **140 mg/g** |
| **Water content** | **<0.2%** |
| **Melting point** | **152°C** |
| **Klett colour index** | **max. 40** |
| **Average particle size** | **75 µm–95 µm** |
| **Bulk density** | **500 ±50 kg/m³** |
| **pH value [1% in deionized water]** | **approx. 5** |
| **Solubility in water at 20°C** | **approx. 2 g/l** |
| **Dust explosion class** | **ST 1** |

*Fig. 8* *Physical data of PERACTIVE powder*

## Water solubility

The solubility of PERACTIVE in cold water is approx. 1.5 g/l. This value is far above the maximum usual concentration of the activator used in detergents and cleaning agents (normally 0.2–0.5 g/l). Complete solubility and the optimum use of the activator is guaranteed when used in accordance with instructions over the whole temperature range of 10–90°C. Aqueous solutions of PERACTIVE are only stable to a limited extent on account of the tendency towards hydrolysis.

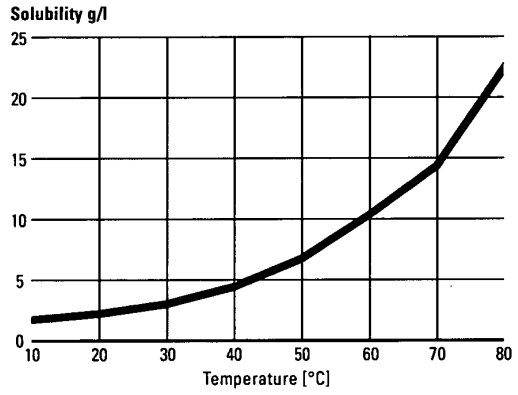



*Fig. 9* *Water solubility of PERACTIVE powder in relation to the temperature, method: gravimetry*

## Dissolution rate

Below the solubility limit PERACTIVE is rapidly soluble even at 20°C. Complete dissolution free of residues is guaranteed within a minute in mechanically agitated systems (washing drums). The dissolution rate is essentially influenced by the particle size of the PERACTIVE powder used.

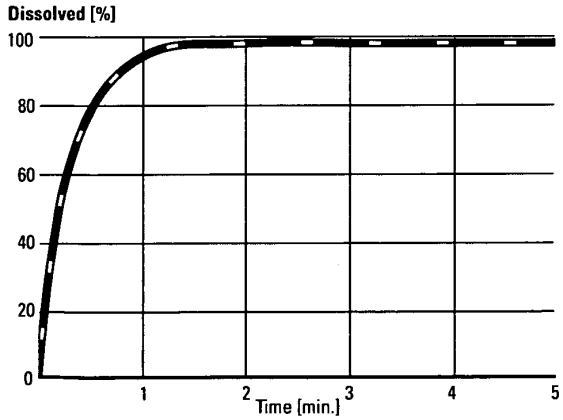



*Fig. 10* *Dissolution rate of PERACTIVE powder at 20°C, method: gravimetry*



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# PERACTIVE –
## Optimization of the bleaching process

Active oxygen bleaching is a complex chemical reaction and takes place in at least two partial stages. In the first stage, perhydrolysis, PERACTIVE reacts with hydrogen peroxide (from perborate or percarbonate). Two molecules of peracetic acid and the easily biodegradable and toxicologically harmless diacetylethylenediamine (DAED) are generated. This reaction takes place in a few minutes in the pH range between 10 and 11 almost independently of the temperature and even at room temperature.

The mechanism, in which the peracetic acid subsequently reacts with the chromophoric systems of the soiling, has not yet been finally clarified. The formation of active oxygen, i.e. the transfer of a peroxide oxygen atom of the peracid and therefore the bleaching result, are influenced both by the substrate and also by the pH value. On the one hand singlet oxygen is possible as a bleaching agent, as is the peracid or its anion on the other. The bleaching reaction itself is a first order reaction in regard to the oxidizing agent and highly dependent on the temperature in the range of 20 to 50°C. Another crucial factor for a good bleaching result is the approach rate of the peracid to the soiled fibre surface.

0.67 g peracetic acid (or 0.14 g active oxygen) is released per gram PERACTIVE. According to the stoichiometry the PERACTIVE : perborate tetrahydrate weight ratio should be 1 : 1.35, when using monohydrate 1 : 0.9. However, in practice a small excess of persalt is necessary to balance its activity losses during storage and decomposition as a result of the interaction with the enzyme catalase and to ensure the optimum use of both components across all washing temperatures. The peracetic acid formed is itself insensitive to catalase.
5% by wt. PERACTIVE are therefore recommended to activate 8–10% by wt. PB*1 or 12–15% by wt. PB*4.

When using the less stable percarbonate its proportion in the formulation should be 10–15% by wt. PERACTIVE quantities <50 mg/l washing liquor do not produce any appreciable bleaching action, an increase up to 500 mg/l is associated with a constant increase in the degree of whiteness.

The optimum bleaching result is achieved, if the pH value at the beginning of the washing process is initially between 10 and 11, to guarantee optimum perhydrolysis, and is subsequently reduced to values between 9 and 10 to obtain the best possible bleaching effect.



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# Part I: Perhydrolysis

## Mechanism of the perhydrolysis

On dissolving the persalts in water, hydrogen peroxide is released, which rapidly dissociates under the alkaline conditions of the washing liquor. The formation of perhydroxyl anions necessary for the perhydrolysis stage is promoted by a high pH value (pKa $H_2O_2$ : 11.3). Two molecules of peracetic acid are released by nucleophilic attack of the $OOH^-$ ions on the instable imide bonds of the TAED molecule in PERACTIVE. Since the perhydrolysis takes place much more quickly than a hydrolysis reaction, this side reaction can be largely excluded, providing the pH value is below 11. The formation of diacyl peroxide is not observed when using PERACTIVE.

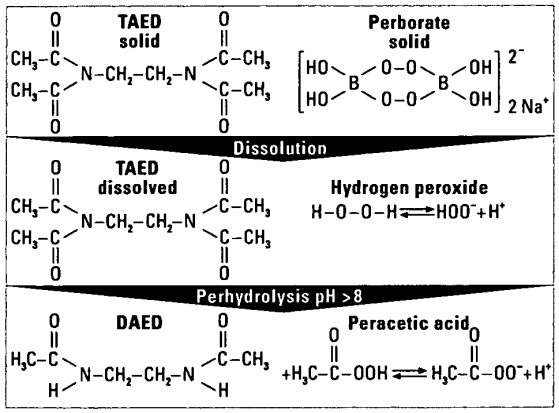



*Fig. 11* *Reaction mechanism of bleaching*

## Closer examination of the reaction mechanism

Computer simulations, based on rate constants of the perhydrolysis ($k_1$) and the formation of active oxygen ($k_2$) determined experimentally, provide a detailed insight into the course of the reactions of the PERACTIVE system which take place in the washing liquor. The degree of perhydrolysis is usually over 95%, the peracetic acid formed is largely stable in the absence of a reaction partner (substrate).

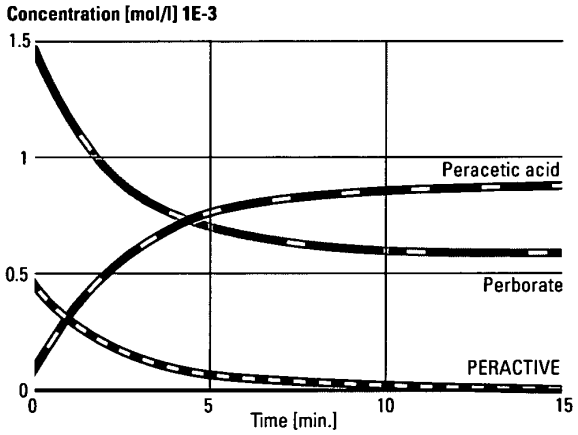



*Fig. 12* *Bleaching reaction in schematic form*

## Reactivity of perborate with PERACTIVE

The reaction of perborate with PERACTIVE can be followed by means of the decrease in the persalt concentration. In the neutral pH range perborate reacts only very slowly with PERACTIVE at 22°C. pH values between 7.5 and 8.5 can be advantageous, if the delayed release of peracid over several hours is required. This may be the case for example for certain soaking or disinfectant processes. pH values >9.5 are advisable for use in detergents.

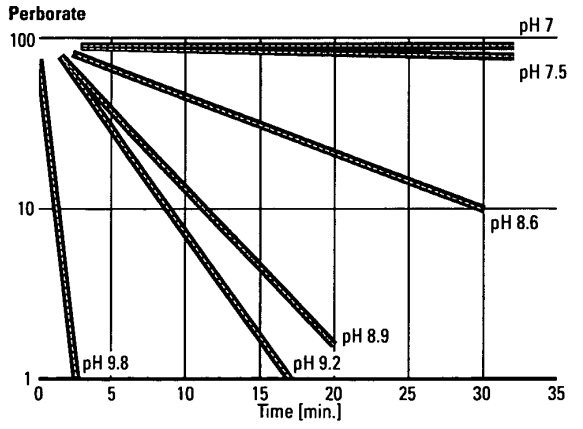
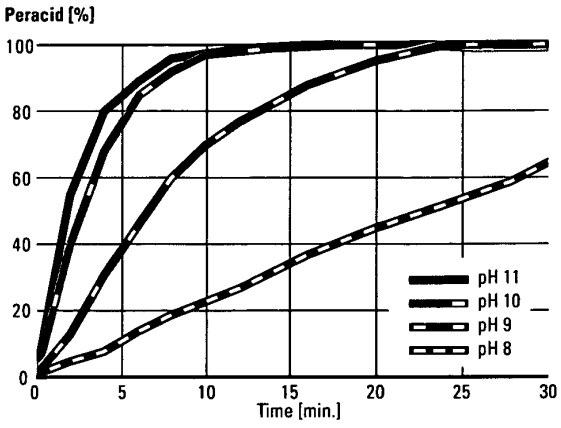



*Fig.13* *Influence of the pH value on the reaction of perborate with PERACTIVE at 22°C*



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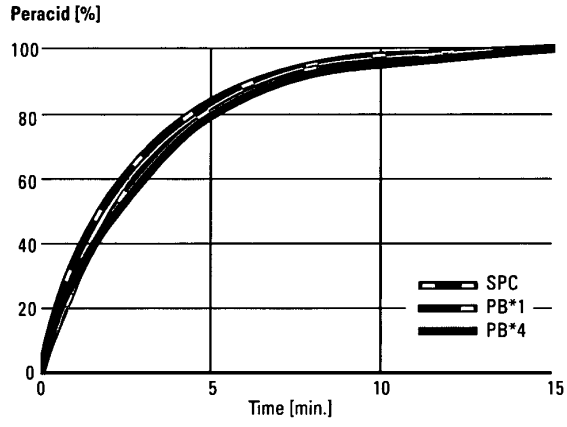



*Influence of the pH value on the peracid formation at 20°C*
*8 g/l WMP/ 1.5 g/l PB*4/ 0.5 g/l PERACTIVE powder*

*Fig. 14*

## pH dependence of the peracetic acid formation

The formation of peracid can be controlled over wide limits by means of the pH value of the washing liquor. In the optimum pH range between 10 and 11 the perhydrolysis is almost independent of the temperature and even at 20°C it is completed within a few minutes.

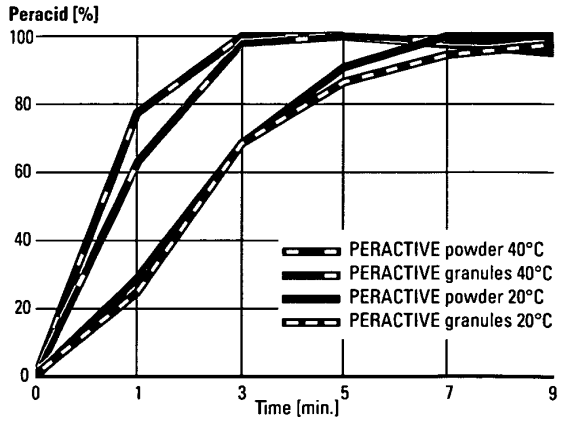



*Influence of the type of persalt on the peracid formation at 20°C.*
*8 g/l WMP/ 1.5 g/l persalt/ 0.5 g/l PERACTIVE powder*

*Fig. 15*

## Influence of the type of persalt

PERACTIVE can be combined with a large number of persalts. There are only insignificant differences in reactivity between the perborates and percarbonate. The slightly faster reaction with percarbonate can be attributed to its higher pH value (around 10.7) compared to perborates (around 10.2). Furthermore, PERACTIVE can also activate other hydrogen peroxide donors such as urea adducts. Activation of Caro's acid or its salts ($KHSO_5$) is not observed.




*Peracid formation at 20 and 40°C*
*8 g/l WMP/ 1.5 g/l PB*4/ 0.5 g/l PERACTIVE powder or granules*

*Fig. 16*

## Reactivity of PERACTIVE granules vs. PERACTIVE powder

PERACTIVE is used in washing powders only in granulated form to increase the stability in storage. The granulation auxiliary agents used ensure rapid dissolution in the washing liquor, so that even at 20°C the release of peracid is only retarded imperceptibly compared to that of the powder.



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# Part II: Active oxygen formation and bleaching

## Mechanism of the active oxygen formation

Following perhydrolysis the transfer of an oxygen atom of the peracid to the substrate to be bleached is the second stage of the bleaching process. Conceivable intermediate steps for this process are singlet oxygen, the formation of which is observed in particular in the vicinity of the pKa of peracetic acid (pKa=8.3), or mesomeric resonance structures of the peracetic acid or its anion. The bleaching result is influenced largely by the reactivity of the peracid, not by the rate of its formation.

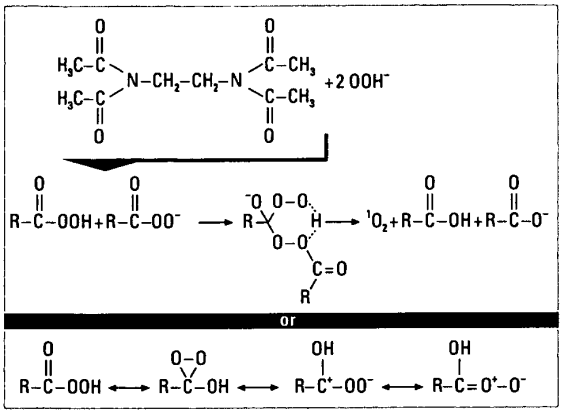



*Fig. 17* *Mechanism of the active oxygen formation*

## Reactivity towards different stains

PERACTIVE is effective on a large number of different types of stains. Excellent results are obtained in particular with hydrophilic stains such as tea, coffee or red wine. However stubborn, more hydrophobic stains such as grass, juices and spices or cocoa stains containing protein can also be destroyed by oxidation. The washing result can be additionally enhanced by suitable surfactant combinations or enzymes.

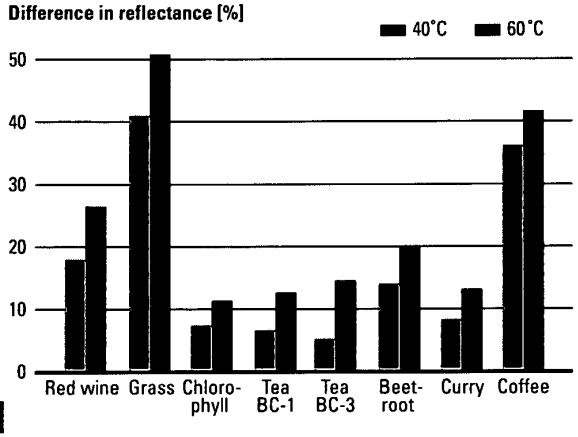



*Fig. 18* *Bleaching results at 40 and 60°C in AEG Eco Lavamat 6753 Sensortronic 100 g detergent incl. 8% SPC and 3% PERACTIVE*

## Time dependence of the bleaching

The bleaching effects attainable are dependent on time and temperature. Furthermore, the type of soiling also plays an important role. In a 60°C wash 80% of the bleachable hydrophilic stains are destroyed by oxidation within the first 30 minutes, and generally even in the first 15 minutes. At room temperature the reaction takes place more slowly, the time factor playing an important role. Here too, however, considerable effects are visible in the first half hour after the addition of the bleaching system.

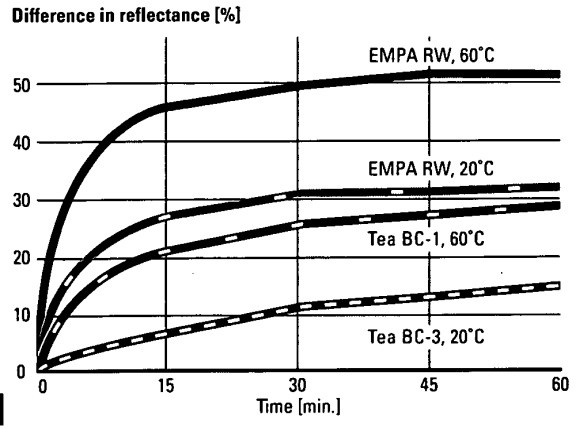
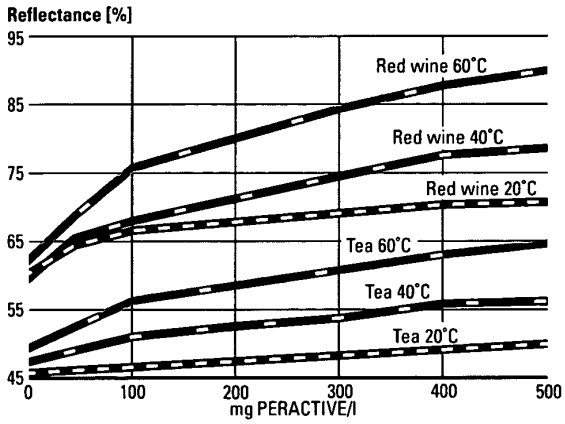



*Fig. 19* *Time dependence of bleaching at 20 and 60°C on tea and red wine 5 g/l detergent incl 10% PB*1 and 5% PERACTIVE, 15° water hardness*



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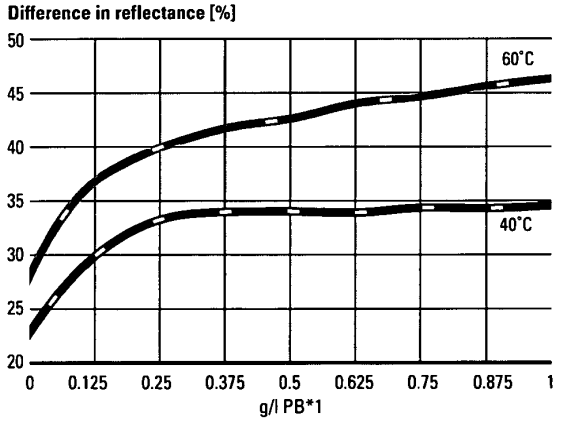



*Dependence of bleaching action on the PERACTIVE concentration*
*5 g/l detergent, weight ratio PERACTIVE : PB*1 = 1 : 2*
*15° water hardness, 30 min.*

*Fig. 20*

## Influence of the PERACTIVE concentration

Critical for a convincing bleaching result is the concentration of PERACTIVE in the washing liquor, which is determined by the PERACTIVE content in the washing powder and its dosage. Only slight effects are visible at PERACTIVE concentrations below 50 mg/l. Concentrations of 100–400 mg PERACTIVE/l washing liquor are normally used. Higher concentrations only lead to marginal improvements in the bleaching result, but may be advantageous for stubborn stains–especially in the soaking process.

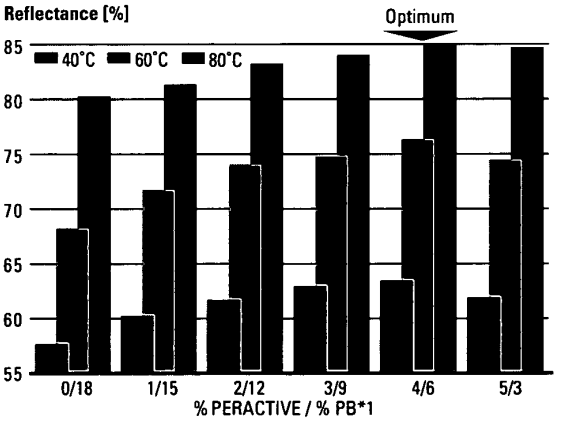



*Influence of the persalt concentration on the bleaching on red wine*
*5 g/l detergent incl. 5% PERACTIVE, 15° water hardness, 30 min.*

*Fig. 21*

## Optimum persalt concentration

An activator : perborate monohydrate weight ratio of around 1 : 1 is necessary for the effective use of PERACTIVE, as shown by washing experiments at 40°C. No additional bleaching effect is observed at this temperature even with large persalt excesses. With the 60°C wash on the other hand excess perborate contributes to an improvement in the result.




*Optimization of the PERACTIVE : perborate ratio*
*Mean value from 7 stains / 7.5 g IEC/l (incl. bleaching system)*

*Fig. 22*

## PERACTIVE : persalt ratio

Partial substitution of perborate, which is not very effective at temperatures below 60°C, by PERACTIVE produces significantly better bleaching results on various types of stains over the whole temperature range. An optimum result is shown for a PERACTIVE : PB*1 ratio of 4 : 6, which is clearly superior to a conventional system with 2 PERACTIVE and 12 PB*1 even at 80°C. Bleaching reserves in the form of excess persalt are therefore not necessary for the boil wash.



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## pH dependence of the bleaching of hydrophilic stains

Bleachable hydrophilic stains in the pH range 8–10 are removed particularly well using the PERACTIVE system. The respective bleaching optimum is specific to the substance.

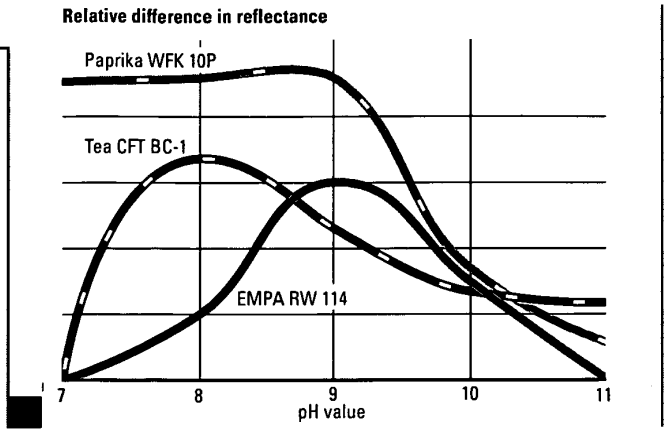



*Fig. 23*

*pH dependence of the bleaching at 40°C*
*400 g $H_2O$/ 1.6 g WMP/ 0.36 g PB*4/ 0.08 g PERACTIVE powder*
*Glass beaker experiments: 30 min., 15° water hardness*

## pH dependence of the bleaching of hydrophobic stains

Hydrophobic stains are generally more difficult to bleach than hydrophilic stains. It is possible to assist the bleaching process by using suitable enzymes, surfactant combinations or by means of a pH value of 9.5–10.5.

In order to achieve as wide a spectrum of activity as possible of the PERACTIVE system, the (final) pH value of the washing liquor should be around 9.0–9.5. In this way both hydrophilic and hydrophobic soiling can be bleached effectively.

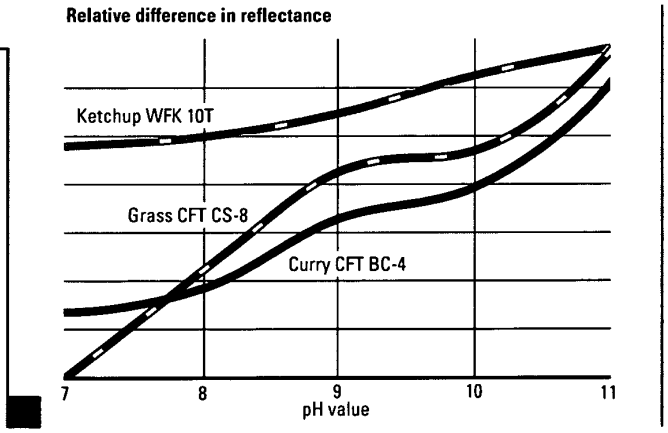



*Fig. 24*

*pH dependence of the bleaching at 40°C*
*400 g $H_2O$/ 1.6 g WMP/ 0.36 g PB*4/ 0.08 g PERACTIVE powder*
*Glass beaker experiments: 30 min., 15° water hardness*

## Optimum pH control

The pH value of the washing liquor has a significant influence on the bleaching result. For the optimum use of the PERACTIVE system it should be 10.5 at the beginning of the washing process to ensure the fast and complete formation of the peracid. The subsequent reduction to pH values below 10 promotes the bleachability of most stains. This pH control takes place automatically in unbuffered detergents containing PERACTIVE, in that the peracetic acid formed is converted into acetic acid. The pH profile for most detergents can be controlled by the addition of suitable acid compounds (citric acid, sodium hydrogen carbonate).

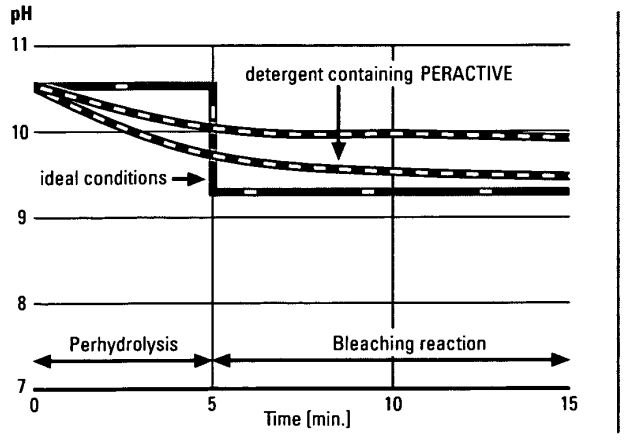
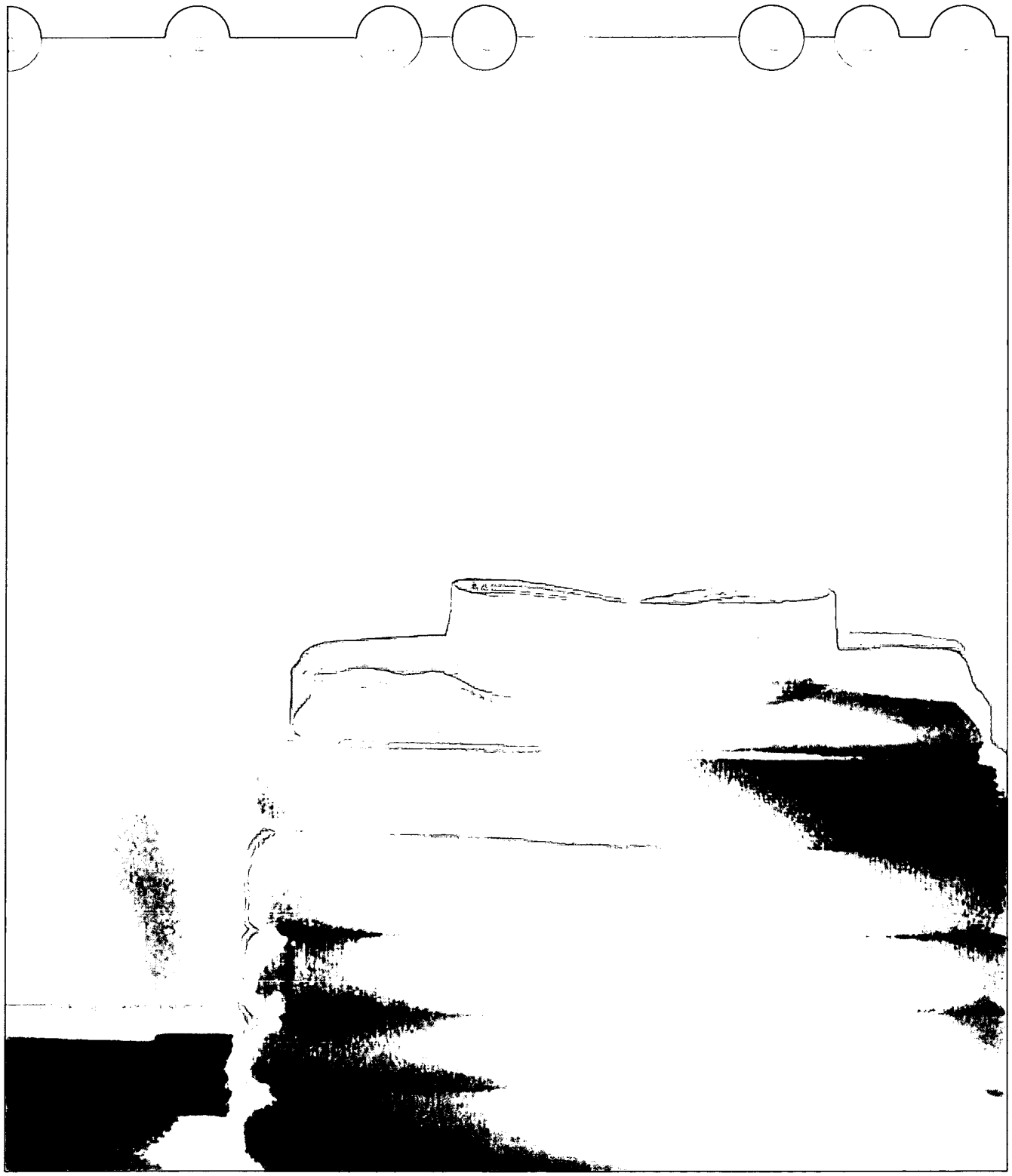



*Fig. 25*

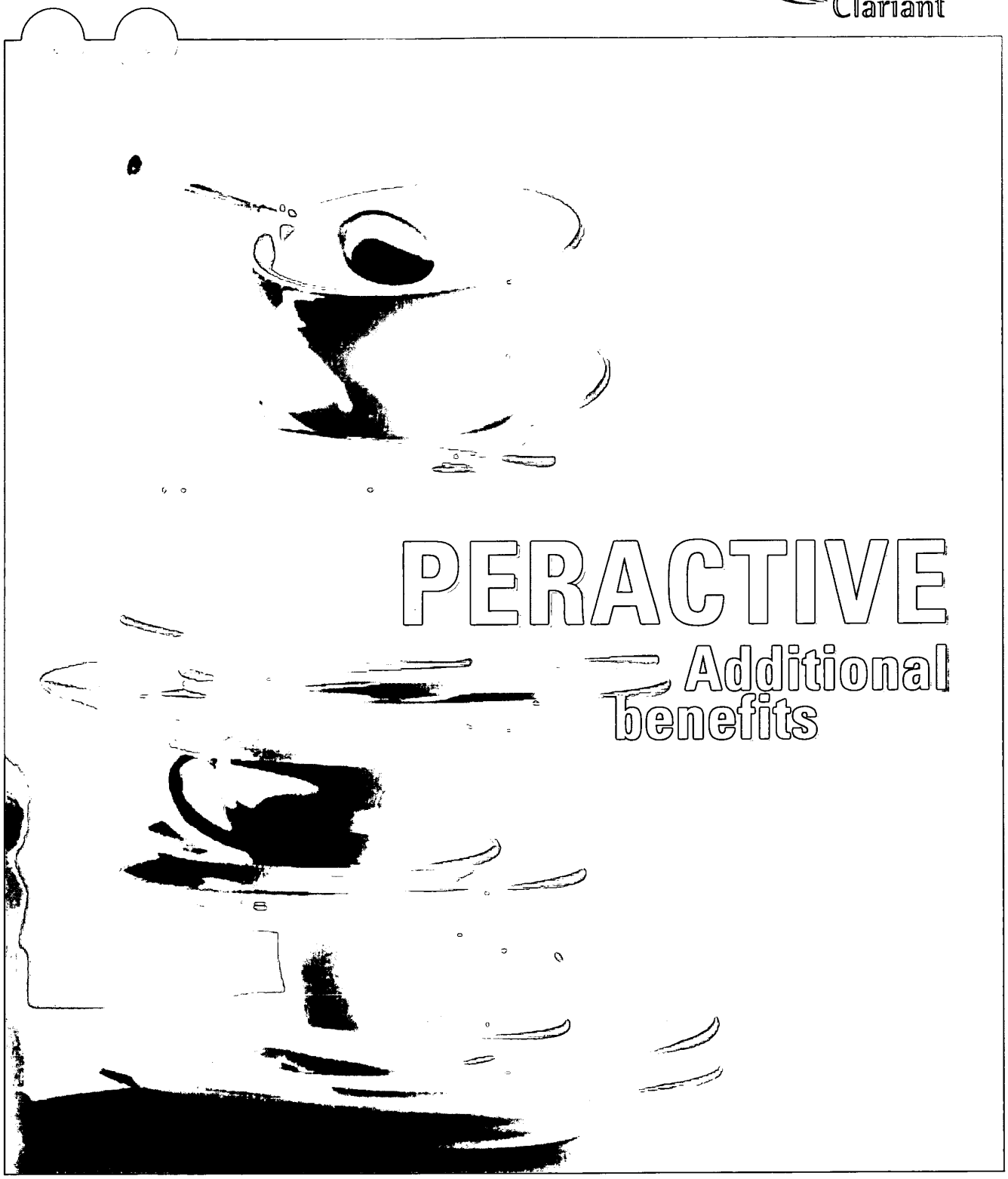
*pH profile of the bleaching reaction*



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Clariant



# PERACTIVE

## Additional benefits

# PERACTIVE –
## Hygiene and deodorization

Bacteria and other microbial germs do not only occur as pathogens, but are also responsible for the formation of sweat and the production of unpleasant odours. In the past the microbes adhering to the laundry were destroyed completely by the heat during the boiling wash. In modern detergents the bleaching system fulfils this function at much lower temperatures. The destruction of bacteria, germs and unwanted odours results in a "hygienically clean" 40°C wash corresponding to the standard of the boiling wash.

The antimicrobial action of peracetic acid and of hydrogen peroxide has long been known. Whilst peracetic acid displays effective bactericidal, viricidal and fungicidal properties, hydrogen peroxide has a particularly antiseptic and bacteriostatic action. Its sporicidal properties are also to be emphasized. Both supplement each other ideally. Both perborates and percarbonate are suitable as a source for hydrogen peroxide.

In the absence of a bleaching system a large number of germs survive in the washing liquor or on the laundry at washing temperatures below 60°C. 95% of the microorganisms are destroyed by the persalt, but destruction rates of >99.99% are achieved only by the addition of PERACTIVE.

Even at washing temperatures below 40°C, where the activity of hydrogen peroxide – in particular with short washing cycles – is not very good, the efficiency can be improved by using PERACTIVE and the spectrum of activity can be broadened considerably. Systems containing PERACTIVE are therefore also used in disinfectants and cleaning agents with antimicrobial action (denture cleaners).

In addition to the germicidal action, odours adhering to the laundry such as kitchen and tobacco odours or sweat are destroyed by the bleaching system. Here too, the effectiveness can be clearly enhanced by PERACTIVE. This is particularly important in perfumefree detergent formulations.



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## Biocidal efficiency of the PERACTIVE system

The PERACTIVE system displays excellent effectiveness towards a wide spectrum of pathologically active germs. This is true especially with low application temperatures and short reaction times. At room temperature no significant effect is established with percarbonate or PB*1 or PB*4 alone. The addition of PERACTIVE results in effective destruction (>99.99%) even with contact times of less than 15 minutes. This is particularly of interest in countries with cold wash conditions or for the use in disinfectants.

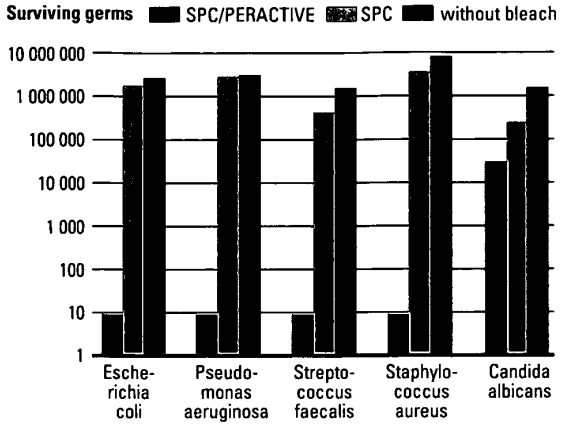



*Fig. 26* *Sterilization by SPC/PERACTIVE in the washing liquor at 25°C 300 mg/l SPC/ 200 mg/l PERACTIVE, 15 min.*

## Also effective against yeast fungi

The yeast fungus candida albicans proves to be particularly stubborn when treated with oxygen releasing disinfectants. Its growth is hardly impaired by detergents without any bleaching system. Even at 40°C the addition of PB*1 alone does not lead to the desired effect. A significant reduction in germs even at 40°C can be achieved, however, by adding 3–5% PERACTIVE.

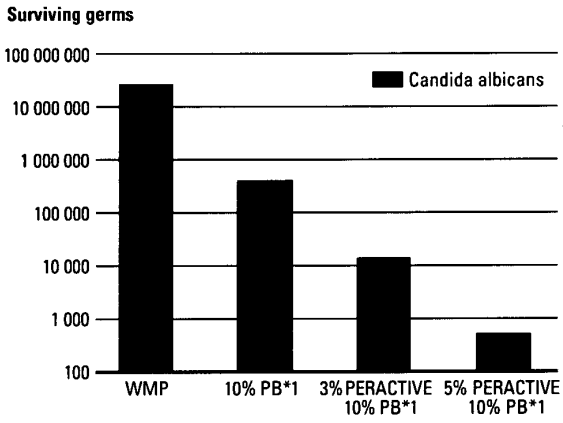



*Fig. 27* *Sterilization in the washing liquor at 40°C 5 g/l WMP, 45 min.*

## Elimination of unpleasant odours

Bacteria can be deposited together with the soil on the laundry or on hard surfaces and spread an unpleasant odour as a result of their metabolic products. By using detergents and cleaning agents containing the PERACTIVE system these odours are also destroyed by oxidation and therefore neutralized. The same is true of typical cooking smells (food) or tobacco smells. Detergents containing the PERACTIVE system were judged by far the best in the panel test.

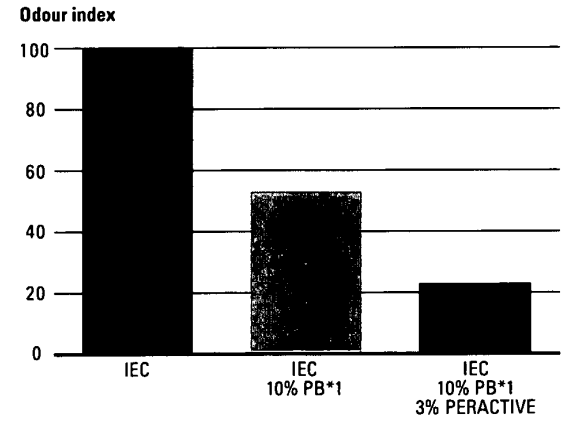



*Fig. 28* *Odour neutralization at 30°C after 15 min. 5 g/l IEC, panel test, 30 persons, mean value from 5 odorous substances*



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# PERACTIVE –
## Gentle on colours and fibres

High quality textiles with valuable colourings make laundry a precious item. Their long-term preservation is therefore of particular interest. Their quality should not deteriorate despite frequent washing, the colours of dyed fabrics should not fade and become unsightly.

Laundry can be damaged in many ways. The fading and bleeding of dyes as well as the transfer of dyes are important in practice. In particularly bad cases these processes may lead to the laundry being completely damaged.

Chlorine bleaching is not very suitable for bleaching dirty coloured laundry and delicate fabrics on account of its aggressiveness. Although hydrogen peroxide is far milder, its effectiveness on stubborn stains is not sufficient in the coloured wash. Detergents and bleaching agents containing PERACTIVE on the other hand guarantee the optimum bleaching result at the same time as the best possible care of the textiles. There is no fear of the dyes fading, i.e. the chromophore system of the dye molecules being destroyed by oxidation, using typical concentrations of the PERACTIVE. Most dyes proved inert towards peracetic acid.

The cause of the bleeding is the detachment of dye particles from the fabric, which may result in colour changes or the fading of coloured textiles. Frequently the surfactant or builder combination is responsible for this, not the bleaching system. Furthermore detached dye particles may be deposited on other textiles during the washing process and discolour the fabric. Modern detergents often contain inhibitors, mostly on a polymeric base, to suppress this dye transfer. The function of these additives can be taken over by the PERACTIVE system to a certain degree, by the peracetic acid which has been formed bleaching the detached dyes in the washing liquor and making them invisible.

Another damage caused by washing, although seldom observed, is spotting. This involves partial fading of a dye in the form of dots, caused by an excessive concentration of bleaching agent locally. This may be the case for example with improper soaking, if a high concentration of bleaching agent is deposited on the fabric, without the washing liquor being agitated sufficiently. Undesired spotting can be prevented effectively by using suitable PERACTIVE granules.

In rare cases damage to the fibres in the form of tears or holes can be seen after frequent washing. The reason for this is generally catalytic decomposition of the hydrogen peroxide, caused by traces of metal ions, which get into the washing liquor through the water or the soil on the laundry. The hydroxyl radicals released split the cellulose fibres forming oxycellulose, which results in a decrease in the average degree of polymerization of the cotton and a loss of tensile strength. Additions of sequestering agents or silicates (e.g. SKS-6) to the detergent formulation are suitable for preventing catalytic damage. A reaction of the PERACTIVE with the cotton fibre is only observed to a lesser degree in the boiling wash and does not cause any significant damage to the fibres even with frequent washing.



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## Preservation of the colour

Most classes of dyes behave inertly towards detergents containing PERACTIVE. Neither any lightening or change in shade is observed. There are no interactions with the persalt with the 40 and 60°C wash, the addition of PERACTIVE causes no negative effects either. However, the consumer should check the colour fastness of coloured textiles prior to washing, particularly when using bleach boosters.

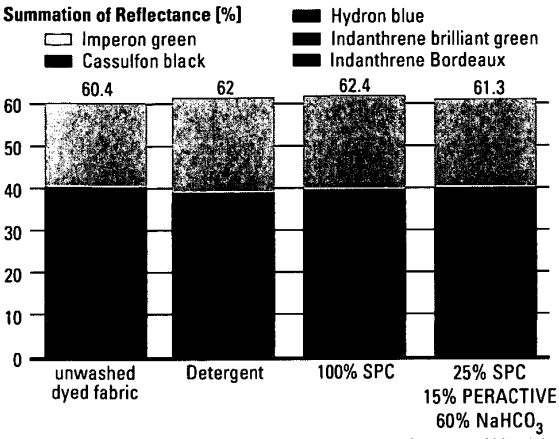



Fig. 29

*Bleaching performance of bleach boosters containing SPC on dyed fabrics at 40°C in the launderometer Cotton stockinet, 2.8 g/l WMP, 2 g/l bleach booster*

## Dye transfer inhibition

PERACTIVE is an expedient addition to dye transfer inhibitors. Peracetic acid attacks the detached dye molecules sensitive to oxidation in the washing liquor and thus prevents any discolouration of neighbouring textiles. This is particularly the case with the 60°C wash.

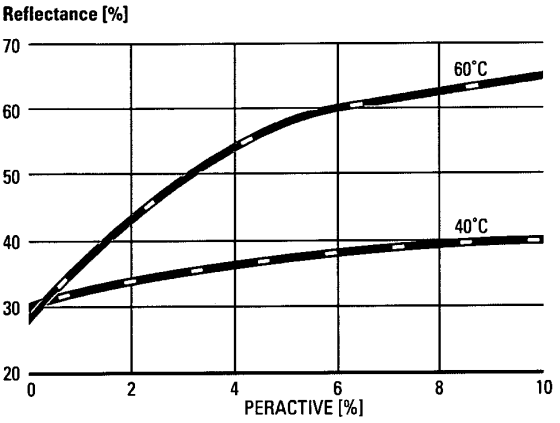



Fig. 30

*Dye transfer inhibition 4 g/l WMP, 15% PB*1, 0.5% Remazol brill. red GG powder, 15° water hardness on white cotton stockinet*

## Protection of the fibre

The PERACTIVE system shows only slight reactivity towards the cellulose fibres of the cotton. Even with frequent washing only minimal damage to the fibres is observed, i.e. a decrease in the average degree of polymerization [DP value], which does not represent any significant reduction in the serviceability of the textiles. Genuine damage to the fibres on the other hand is caused by traces of metal ions.

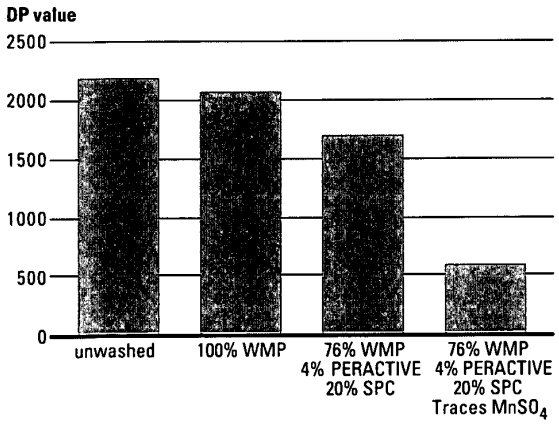



Fig. 31

*Average degree of polymerization after 25 washes at 40°C in LINI test, 8 g/l detergent*



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Clariant



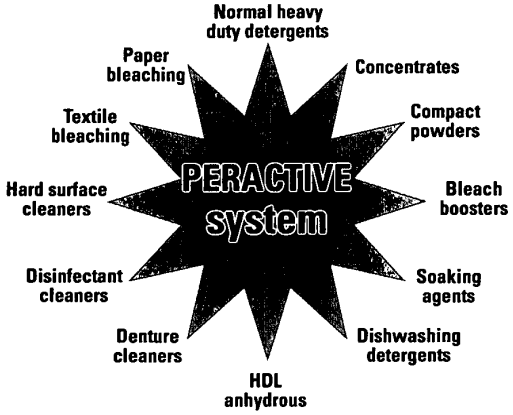
# PERACTIVE

## Applications

# PERACTIVE –

## A bleaching activator with numerous application possibilities

There are numerous applications for PERACTIVE. It can be used both for the activation of perborates (monohydrate or tetrahydrate) and also percarbonates (stabilized or unstabilized). It is compatible with all the commercial ingredients of modern detergents and cleaning agents. Particularly sensitive components such as enzymes, optical brighteners and perfume oils are in the meantime available in PERACTIVE compatible variants. As a solid it is particularly suitable for use in products in powder form. It is generally used in granulated form to improve its handling, suppress the interaction with other ingredients and increase stability in storage. Various types of granules, optimized for the relevant field of application, can be obtained commercially.




*Possible uses of PERACTIVE* *Fig. 32*

The main fields of application for the PERACTIVE system are the conventional, concentrated and compact heavy duty detergents, as well as bleach boosters and dishwashing detergents. It displays optimum effectiveness in the temperature range of 30–60°C. Use in liquid products is still in development, since in this case greater demands are made on the storage stability of the PERACTIVE system. Sufficient stability can be obtained in anhydrous liquid systems. The sterilizing action of PERACTIVE is valued above all in denture cleaners and cleaning agents for hard surfaces. PERACTIVE powder in the form of anhydrous suspensions makes simple dosage possible for industrial laundries. Additional potential areas of application are textile and paper bleaching, where initial positive results were obtained for the substitution of chlorine bleach by the PERACTIVE system.

Washing habits and detergents differ throughout the world. Whereas in Europe washing is carried out predominantly at 30–60°C, occasionally even at 95°C, in the USA and the Far East washing is done at much lower temperatures and with far shorter washing times. In addition washing by hand is common in many countries and the washing is also frequently pretreated over night by soaking.

In the vast majority of cases the use of PERACTIVE has a positive effect – independent from the washing temperature. However, for the system to be used effectively the formulation has to be optimized with regard to the washing habits typical for that country. The toxicological and ecotoxicological safety of PERACTIVE guarantees protection for the processor, the user and the environment if processed properly.



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# PERACTIVE

## in modern heavy duty powder detergents

The European detergent market has undergone a number of innovations in recent years:

- New production processes such as agglomeration or extrusion enable more compact products to be made with bulk densities between 600 and 900 g/l permitting reduced dosage and savings in packaging materials.

- New ingredients such as percarbonate, layered silicates, sugar surfactants or enzyme mixtures result in improved formulations which are more effective in terms of volume and help to safeguard the environment.

- New washing machines use water and energy in the optimum manner. Greater use of the gentle washing process or of multichamber dispensing systems result in energy saving and optimum use of all the detergent ingredients.

PERACTIVE can be used in all types of commercial powder detergents (normal, concentrated and compact) without any problems and is compatible with the other ingredients. It can be combined with all builder systems [zeolite, layered silicates or phosphate]. It can be used either for the activation of cost-effective sodium perborate tetrahydrate, the monohydrate which is more effective in terms of volume or the environmentally friendly percarbonate. The stability of the persalts in storage is not affected negatively by the presence of PERACTIVE.

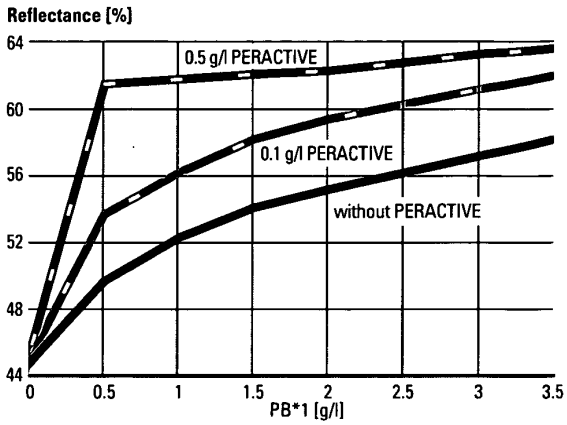
PERACTIVE is normally used in granule form in detergent formulations. They ensure excellent stability in storage, prevent interaction with sensitive detergent components and guarantee optimum utilization during the washing process. PERACTIVE granules are easy to process, low in dust and free flowing. In order to ensure the greatest possible flexibility on processing, the PERACTIVE granules normally are not given any further additives besides granulating auxiliary agents and coating materials. When incorporated properly into suitable formulations they also ensure an excellent stability even after a longer storage period.

The PERACTIVE system should be adapted to the relevant formula. In addition to the concentration of the bleaching system the pH value of the resultant washing liquor is of crucial importance in order to obtain the best possible effect. It can be controlled by the use of pH regulators.

The use of multi-active PERACTIVE makes it possible to produce more effective bleaching systems in terms of volume with a reduced percentage of persalt and excellent low temperature bleaching efficiency without any losses in the boiling wash. A further reduction in volume of the detergent can be achieved by the incorporation of layered silicates (e.g. SKS-6), which are effective as builders, alkali sources, heavy metal ion binders and surfactant carriers. PERACTIVE is also highly effective in these formulations.



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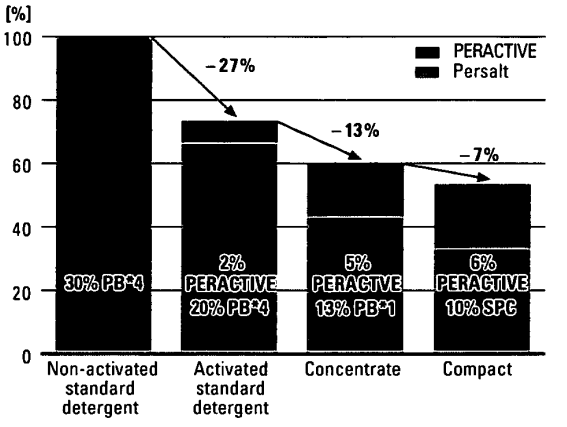



*Improvement in performance by means of PERACTIVE*
*LINI test, 40°C, 30 min., 5 g/l WMP, in addition bleaching system, mean value tea/red wine-staining*

*Fig. 33*

## Significant increase in performance as a result of using PERACTIVE

By adding 0.1 g/l PERACTIVE and 1.0 g/l perborate the same bleaching effect can be obtained as with 2.5 times of the non-activated persalt. Activated formulations therefore enable significant savings in persalt to be made (saving in volume) with the same or better bleaching efficiency. The discharge of chemicals into the environment can therefore be reduced considerably. More cost-efficient bleaching systems can be produced with PERACTIVE by means of suitable formulations.




*Reduction in volume as a result of activated bleaching systems*

*Fig. 34*

## Significant reduction in volume with activated bleach systems

The use of PERACTIVE makes it possible to reduce the volume of the bleaching system by about 50%. The successive replacement of excess perborate by PERACTIVE is the first stage, without any reduction in performance. The use of the more volume-effective perborate monohydrate instead of tetrahydrate leads to an additional reduction in volume. The combination of environmentally friendly percarbonate with PERACTIVE is economically and ecologically the most expedient solution of a bleaching system for compacts.

| PERACTIVE-Content | |
|---|---|
| Conventional detergent | 1–3% |
| Concentrate | 3–6% |
| Compact | 4–8% |

| PERACTIVE : Persalt ratio | PERACTIVE : Persalt |
|---|---|
| Sodium perborate tetrahydrate | 1 : 2–3 |
| Sodium perborate monohydrate | 1 : 1.6–2.2 |
| Sodium percarbonate | 1 : 2–3 |

| pH values of the washing liquor | |
|---|---|
| At the start of the washing process | 10–11 |
| During the washing process | 9–9.5 |

*Optimized conditions when using PERACTIVE in detergents*

*Fig. 35*

## Optimized bleaching systems

The concentrations and weight ratios stated are guidelines and have to be optimized if necessary. In unbuffered formulations containing PERACTIVE the lowering of the pH value takes place largely automatically as a result of the acetic acid formed. In buffered systems the use of acid additives with retarded dissolving behaviour is advisable.



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## PERACTIVE in concentrated and compact powders

PERACTIVE granules are eminently suitable for use in concentrated and compact powders. They are generally added to the washing powder towards the end of the production process, to rule out excessive mechanical stress during the mixing process. Optimum stability in storage is ensured in this way. Together with other multifunctional ingredients, such as percarbonate and layered silicates [SKS-6], PERACTIVE makes it possible to produce highly compact powders.

| | | Compact [%] | Concentrate [%] |
|---|---|---|---|
| **Builders** | Zeolite | — | 15–25 |
| | SKS-6 | 40–50 | 10–15 |
| | $Na_2CO_3$ | — | 8–15 |
| | $NaHCO_3$ | 8–12 | — |
| | Na citrate | 0–4 | — |
| **Bleach** | SPC | 10–15 | — |
| | PB*1 | — | 10–15 |
| | PERACTIVE | 6–8 | 4–6 |
| **Surfactants** | Anionic surfactants | 6–8 | 6–8 |
| | Nonionic surfactants | 8–10 | 6–8 |
| **Others** | Polyacrylates | 1–4 | 2–6 |
| | Sequestering agents | 0–1 | 0–1 |
| | Enzymes | 0.5–2.5 | 0.3–2.0 |
| | Miscellaneous | ad 100 | ad 100 |
| | Dosing [g/wash] | 60 | 75 |

*Fig. 36* *Guideline formulations for concentrated and compact powders*

## Builder compatibility

PERACTIVE granules are compatible with all commercial builder systems and also display an excellent degree of conservation after several weeks' storage. However, the builder system has a significant influence on the stability of the persalt. In particular (uncoated) sodium percarbonate rapidly loses activity in formulations containing zeolite. Very good storage stability is guaranteed on the other hand in formulations free of zeolite based on SKS-6.

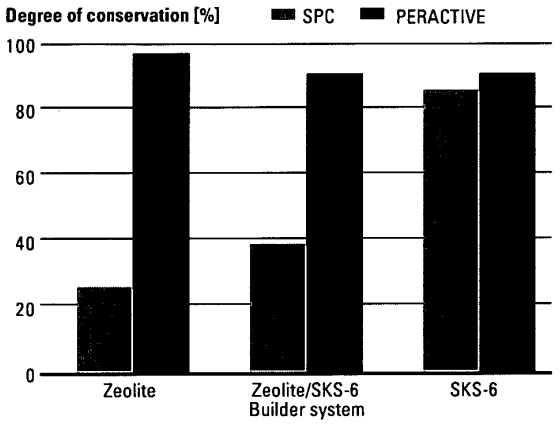



*Fig. 37* *Stability in storage of the PERACTIVE system in the presence of different builders 12 weeks' storage at 30°C in sealed containers*

## PERACTIVE in formulations containing SKS-6 / percarbonate

The change from formulations containing zeolite / perborate to more environmentally friendly detergents based on SKS-6 and percarbonate necessarily involves an increase in the pH value of the washing liquor. As a result there is a shift in the performance spectrum of the PERACTIVE. Whereas slight losses in performance have to be accepted with regard to hydrophilic soiling, the bleaching performance is improved with regard to more hydrophobic types of stains.

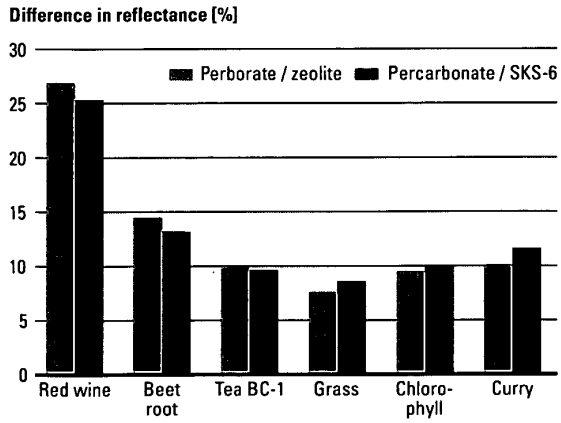



*Fig. 38* *Bleaching performance of PERACTIVE combined with perborate / zeolite vs. percarbonate / SKS-6 at 40°C. 3 g/l detergent incl. 0.5 g/l builder, 0.4 g/l persalt, 0.2 g/l PERACTIVE, 15° water hardness, 30 min. in LINI test*



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# PERACTIVE –
## in bleach boosters

Bleach boosters are increasingly gaining importance as detergency boosters and a component of building block systems. They are used either to pretreat the wash (soaking) or as an additive to the normal detergent, if the heavy soiling of the wash so demands. Combined with light duty or liquid detergents – used specifically and only if necessary – they can totally replace detergents containing bleach and make a significant contribution towards safeguarding the environment.

The main components of all bleach boosters are persalts – generally percarbonate (20–80%) – and PERACTIVE (3–15%). In addition enzymes, surfactants and sequestering agents may be incorporated to enhance the efficiency towards stubborn stains such as grass, fruit or blood stains. The appropriate choice of filler is crucial for the optimum performance of the bleach boosters. This should take over the function of a pH regulator, buffer or stabilizer or as inert material improve the formulation's thermostability.

The full bleaching power of bleach boosters containing PERACTIVE is realized in particular with the 40 and 60°C wash as well as in the soaking process at 20–40°C. Crucial for the efficiency is the pH value of the washing liquor, which is a result of both the basic detergent and the bleach booster. Formulations containing PERACTIVE based on 25% persalt are in most cases clearly superior in performance compared to bleach boosters consisting of pure persalt. A significant additional effect is to be seen in the germicidal action.

Under certain circumstances the bleach boosters can affect the performance of the enzymes of the basic detergent negatively on account of the high content of bleaching agent. Optimum enzyme and bleaching performance is observed by the delayed addition of the bleach boosters (10–15 min. after the start of the wash).

Bleach boosters containing PERACTIVE are characterized by good storage stability. However, it must be noted when choosing the formulation that mixtures of fire accelerating percarbonate with organic materials such as PERACTIVE or surfactants may have a tendency towards exothermic decomposition under unfavourable processing or storage conditions. The processing instructions for persalts and PERACTIVE are to be observed to ensure safe handling. In addition thermochemical investigation of the final formulation is advisable. Special types of PERACTIVE granules for use in bleach boosters can be obtained commercially.



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## Optimized bleaching as a result of optimized additives

The efficiency of the PERACTIVE system can be optimized by the appropriate choice of additives. Whereas the addition of sodium carbonate tends to have a negative effect on the bleaching action, acid substances – in the correct dosage – can increase the bleaching performance. The use of citrate is advantageous, because it assists the bleaching reaction positively.

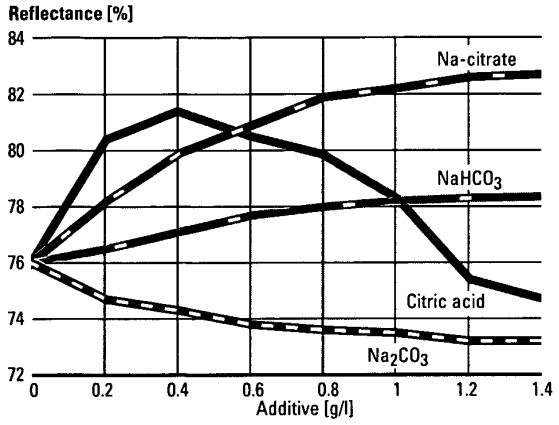



*Fig. 39* *Bleaching system SPC/PERACTIVE at 40°C Influence of various additives* *Red wine staining, 1.5 g/l WMP, 0.5 g/l PERACTIVE, 1.0 g/l SPC*

## Activated and non-activated bleach booster formulations

In the case of bleach boosters without PERACTIVE (non-activated) the addition of an alkaline filler is recommended to assist the bleaching performance of the hydrogen peroxide. In systems containing PERACTIVE the pH value should ideally be between 9 and 10, whereby the activity of the peracetic acid formed can be additionally improved. Additives, like ox-gall soap or sequestering agents, have the effect of increasing the efficiency with regard to certain types of dirt.

| | Non-activated [%] | | | Activated [%] | |
|---|---|---|---|---|---|
| | FS 1 | FS 2 | FS 3 | FS 4 | FS 5 |
| SPC | 100 | 25 | 25 | 25 | 25 |
| PERACTIVE | — | — | — | 15 | 10 |
| $Na_2CO_3$ | — | 75 | — | — | — |
| SKS-6 | — | — | 75 | — | — |
| $NaHCO_3$ | — | — | — | 60 | 40 |
| Citrate | — | — | — | — | 25 |
| pH value | 10.7 | 11.1 | 11.5 | 9.3 | 9.6 |
| Dosing | 2 g/l | | | 2 g/l | |

*Fig. 40* *Formulations of bleach boosters*

## Better bleaching results due to the activated bleach

The performance of different bleach boosters was tested at 40°C combined with different basic detergents, which cover a wide spectrum of the heavy duty, light duty and liquid detergents available on the market. Advantages are clearly revealed for formulations containing PERACTIVE, the performance of which is up to 20% above that of pure percarbonate.

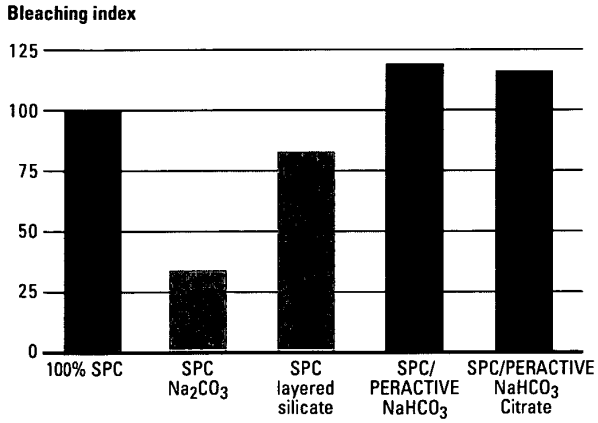
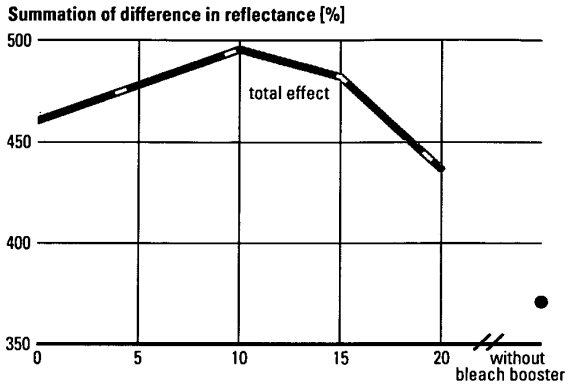



*Fig. 41* *Bleaching results of bleach booster formulations at 40°C combined with 6 different detergents, bleach booster dosing 2 g/l*



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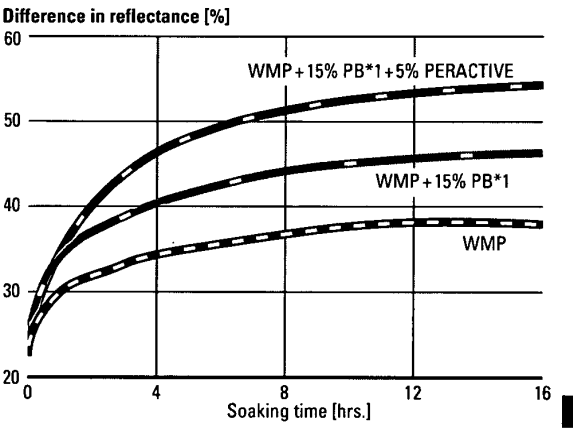



*Bleaching and enzyme effect in relation to the time when the bleach booster is added at 40°C*
*Total of 6 bleachable, 5 protein-containing stains*
*4 g/l WMP incl. 1% enzyme, 2 g/l activated bleach booster, Miele W 723*

*Fig. 42*

## Good enzyme activity with optimum bleaching effect

It is possible to obtain optimum bleaching and enzyme performance by a delayed addition of the bleach booster. The enzymes can therefore fully develop their efficiency at the start of the washing process, whilst the remaining washing time after the addition of the bleach booster is sufficient to remove bleachable stains in the best possible manner. Washing machines with a threechamber dispensing system are particularly suitable for this.

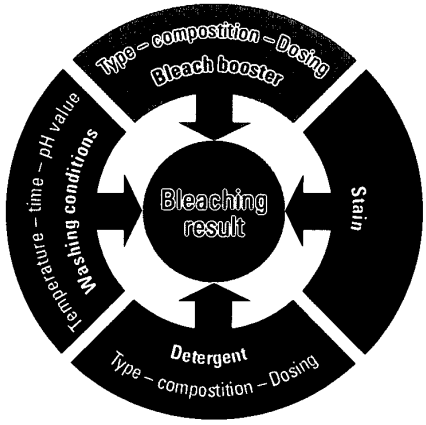



*Pre-soaking tests on tea BC-3*
*Soaking: 5 g/l WMP/ 20°C*
*Washing: 5 g/l WMP/ 15% PB*1/ 40°C/ 30 min.*

*Fig. 43*

## Bleach boosters in the soaking process

Bleach boosters containing PERACTIVE are clearly superior to non-activated formulations in the soaking process at room temperature. Reaction periods of more than 12 hours result in only marginally additional bleach effect.




*Influences on the bleaching result*

*Fig. 44*

## Influences on the bleaching result

Optimization of a bleach booster is generally more difficult than that of a heavy duty detergent. The final bleaching result is not only influenced by the bleach booster, but also by the basic detergent used. The fine adjustment is only possible through the manufacturer, since the latter is able to control the consumer's behaviour with the instructions for use on the package.



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# PERACTIVE
## in denture cleaners

The ingredients of modern denture cleaners are largely substances with cleansing, oxidizing and disinfectant properties. In most cases a complex bleaching system is used consisting of caroate, perborate or percarbonate as well as PERACTIVE. It provides for the necessary hygiene and the fast and complete removal of bleachable soil on the teeth. The cleaning performance is assisted by a mixture of acid components (citric acid or amidosulphonic acid) with sodium carbonate or hydrogen carbonate, which produce an effervescent effect and support the mechanical release of food remains. At temperatures of 30–40°C and reaction times between 10 and 20 minutes the use of a disintegration aid is recommended for faster solubility.

The use of granulated PERACTIVE is recommended for use in denture cleaners to guarantee optimum stability in storage. The typical pH value of the cleaning tablets is in the range of 6–8. PERACTIVE does not display the optimum bleaching action, but particularly in this range the peracetic acid formed proves to be highly reactive towards microorganisms and therefore makes PERACTIVE an indispensable constituent of modern denture cleaning tablets.

| | |
|---|---|
| Sodium perborate x 1 $H_2O$ | 25–35% |
| Potassium peroxomonosulphate | 10–25% |
| PERACTIVE | 2–5% |
| Sodium hydrogen carbonate | 10–20% |
| Sodium carbonate | 5–10% |
| Trisodium citrate | 5–10% |
| Surfactant | 0.5–1% |
| Others (polyethylene glycol, fillers, preservatives, flavouring and colouring matter etc.) | ad 100% |

*Fig. 45* *Formula for denture cleaning tablets*



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# PERACTIVE
## in dishwashing detergents

The increasing number of automatic dishwashing machines suggests a significant growth in the market segment for dishwashing detergents. Not only must dishwashing detergents guarantee the cleanliness and sparkle of the dishes being washed, but also treat the pattern, glass, cutlery and plastic parts with care.

The cleaner component has the task of removing remains of food and dispersing them in the washing solution. Traditional cleaner components contain metasilicates and are consequently labelled as being corrosive. In the past chlorine containing compounds were used as bleaching agents (eg. trichlorocyanuric acid), which are not compatible with enzymes.

The ingredients of modern cleaners are builders (silicates, citrates or phosphates), alkali sources (soda, bicarbonate, silicates), dispersing agents, low foaming surfactants, enzymes and the bleaching agent. The pH value is lowered to 9–11. It is therefore an ideal field of application for the environmentally friendly PERACTIVE system with the usual washing temperatures today of 45–65°C. At the same time it enables highly active proteases and amylases to be used, which assist in removing food containing protein and starch from the dishes being washed.

PERACTIVE is compatible with the ingredients of modern dishwashing detergents. It can be used in formulations both with and without phosphates. It is stable in powder and also in tablet form. 2–6% PERACTIVE are preferably used combined with 5–15% perborate monohydrate or percarbonate to achieve the optimum bleaching result even on stubborn stains such as tea for example. At the same time PERACTIVE suppresses the discolouration of plastic parts, caused by natural dyes in ketchup and food containing curry or paprika. The peracetic acid formed destroys the microorganisms adhering to the remains of the food and ensures that the dishes being washed up are hygienically clean.

The use of PERACTIVE does not have a negative effect on the formation of a coating or glass corrosion. Under certain circumstances however the presence of active oxygen may result in the discolouration of silver cutlery. This involves the formation of layers of silver oxide (possibly also sulphides or chlorides), which are difficult to remove. In this case the optimum formulation of the PERACTIVE system (concentration, ratio PERACTIVE : persalt) as well as the use of silver protective agents (e.g. triazoles or redox systems on an organic or inorganic base) are recommended.



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## Optimized dishwashing formulations

The PERACTIVE system has proved to be the bleaching system of choice in chlorine-free dishwashing detergents. Optimum cleanliness even with stubborn tea stains is achieved whilst safeguarding the environment in the best possible manner. At the same time active oxygen bleaching enables enzymatic systems to be used for optimal stain removal.

| | |
|---|---|
| Sodium disilicate | 20–30% |
| Trisodium citrate dihydrate | 25–35% |
| Sodium carbonate | 5–15% |
| Sodium percarbonate | 5–15% |
| PERACTIVE | 2–6% |
| Surfactant | 1–2% |
| Polyacrylate | 6–8% |
| Protease | 1–2% |
| Amylase | 1–2% |

*Fig. 46* *Formula of a phosphate free dishwashing detergent*

## High cleaning performance due to PERACTIVE

The PERACTIVE system displays optimum activity in the temperature range of 45–65°C. PERACTIVE concentrations of at least 2% are recommended. Parallel to the bleaching performance, the reactivity of the dishwashing detergent towards microorganisms is increased as the PERACTIVE concentrations increase.

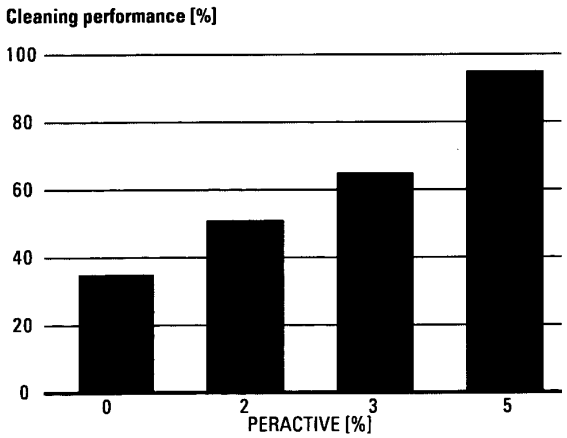



*Fig. 47* *Bleaching results on tea cups*
*Miele, 65°C program*
*mean value of 10 washing cycles*

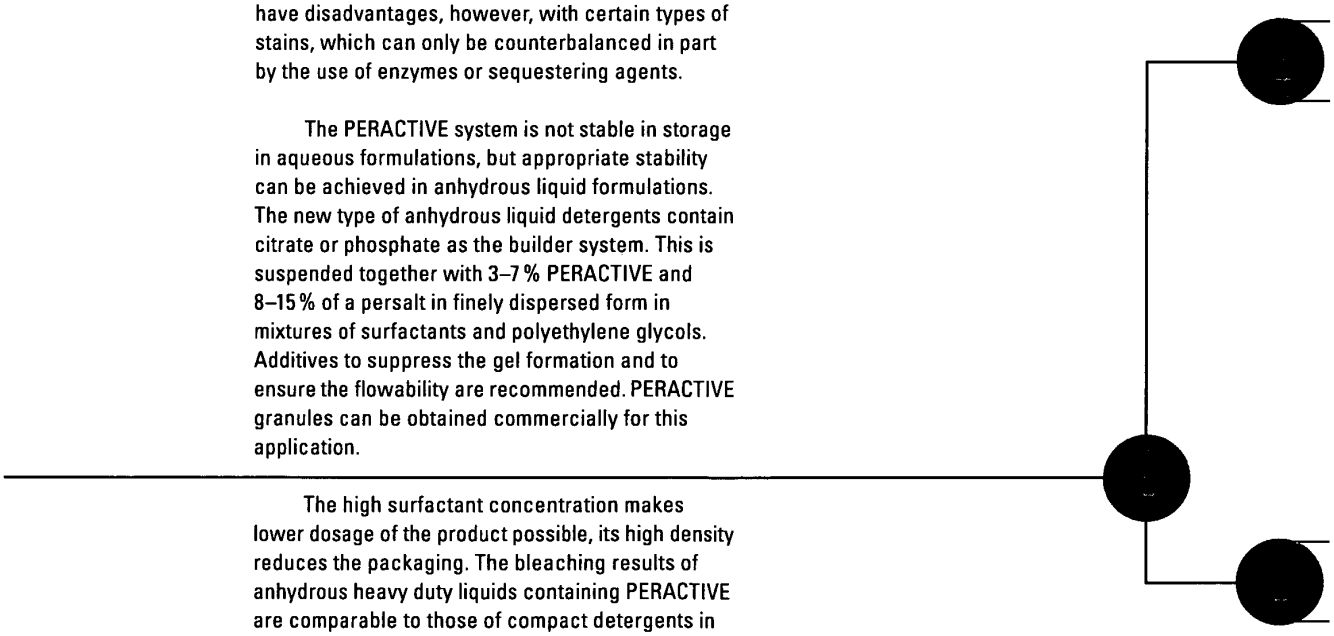


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# PERACTIVE
## in anhydrous liquid detergents

Conventional liquid detergents (heavy duty liquids, HDL) have a number of advantages compared to products in powder form. They are simpler to dispense, they do not produce dust when handling and they dissolve quickly and completely at the beginning of the washing process. As a result of the high surfactant content they are particularly effective against stains containing oil and at low temperatures. Since they do not contain any bleaching system, they have disadvantages, however, with certain types of stains, which can only be counterbalanced in part by the use of enzymes or sequestering agents.

The PERACTIVE system is not stable in storage in aqueous formulations, but appropriate stability can be achieved in anhydrous liquid formulations. The new type of anhydrous liquid detergents contain citrate or phosphate as the builder system. This is suspended together with 3–7 % PERACTIVE and 8–15 % of a persalt in finely dispersed form in mixtures of surfactants and polyethylene glycols. Additives to suppress the gel formation and to ensure the flowability are recommended. PERACTIVE granules can be obtained commercially for this application.



The high surfactant concentration makes lower dosage of the product possible, its high density reduces the packaging. The bleaching results of anhydrous heavy duty liquids containing PERACTIVE are comparable to those of compact detergents in powder form and clearly superior to the conventional heavy duty liquids.



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## Anhydrous formulations enable the use of the PERACTIVE system

PERACTIVE is only stable in anhydrous HDL formulations, since in the presence of water hydrolysis or perhydrolysis occurs immediately with the decomposition of the bleaching system. There is good stability in storage in anhydrous formulations.

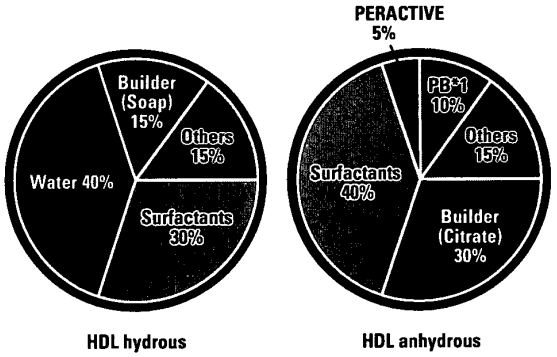



*Fig. 48* *Composition of hydrous HDL and anhydrous HDL*

## Good washing results with low dosages

Liquid detergents with PERACTIVE bleaching system are comparable in performance to conventional powder heavy duty detergents and clearly superior to conventional liquid detergents. Their highly concentrated ingredients contribute in addition towards safeguarding the environment.

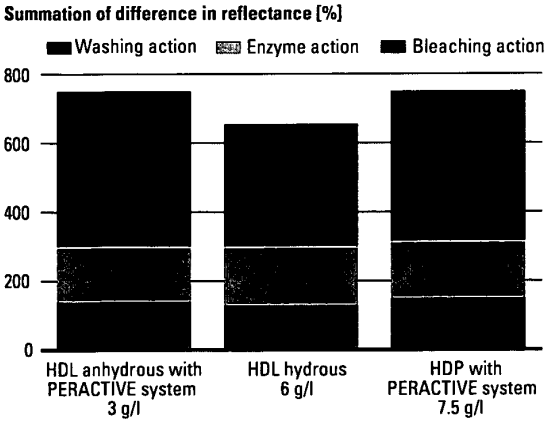



*Fig. 49* *Comparison of the bleaching performance of an activated anhydrous HDL formulation with a HDL without any bleaching system and a conventional heavy duty detergent with bleach at 40°C*



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# PERACTIVE
## in textile bleaching

Sodium hypochlorite and sodium chlorite play important roles as bleaching agents in the textile industry. They are coming increasingly under discussion however in connection with the growing AOX problems. Neither the use of peracetic acid – because of technical problems (instability, odour) – nor its production in situ from acetic anhydride and hydrogen peroxide in the presence of an acid catalyst were successful alternatives. The heat of reaction which is released and the formation of diacyl peroxide as a byproduct make the reaction difficult to control.

The choice of PERACTIVE / hydrogen peroxide as the bleaching system is offered as an alternative. It can be used in the pad batch process, in impregnating bleaching and in the pad steam process. Although bleaching is possible in an acid medium, the best results are obtained in the neutral to weakly alkaline range. The PERACTIVE system offers the following advantages compared to conventional textile bleaching processes:

- The fibres are only damaged insignificantly as a result of the gentle pH value.
- Catalytic damage to the fibres only plays a secondary role.
- The cotton has a supple, soft feel, since waxes and fats remain on the fibre.
- The use of coloured fabrics is possible, as many dyes have less tendency to fade and bleed under these conditions.
- The gentle process is also suitable for bleaching regenerated cellulose.
- Bleaching temperatures <60°C make it possible to save energy.

With pad batch bleaching the maximum bleaching performance of the PERACTIVE / hydrogen peroxide system is in the neutral to weakly alkaline range, preferably between pH 7 and 8.5 at temperatures of 50°C. The cellulose fibre is swollen only a little under these conditions and can be damaged only minimally by the bleaching system.

Impregnating bleaching can be carried out both for a longer period of time (18 hours) at room temperature and also by steaming for a short time (15 min. / 99.5°C). Whilst an optimum pH value of 7.5 is shown for cold bleaching, a maximum degree of whiteness is obtained at pH 10 with hot bleaching.

With the two-stage pad steam process, an optimum between the degree of whiteness and damage to the fibres has to be found. Here the PERACTIVE system can replace the hypochlorite completely. So in the first stage for example the textiles can be padded and steamed with PERACTIVE / hydrogen peroxide and subsequently the peroxide bleaching can be carried out in the alkaline medium (pH 11.5 –12.5). Because for textile bleaching PERACTIVE is partly used in high concentrations, it should be kept in mind that the activator is only moderately soluble in water at room temperature. However, the solubility clearly increases in the range between 40 and 50°C. One part by weight hydrogen peroxide (100%) is capable of activating 3.4 parts by weight PERACTIVE. In practice it is advisable, however, to work with an excess of hydrogen peroxide.



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## The PERACTIVE system in pad batch bleaching

Pad batch bleaching can be carried out under both acid and alkaline conditions. Optimum bleaching results with minimal fibre damage are observed at 50°C in the neutral to weakly alkaline range.

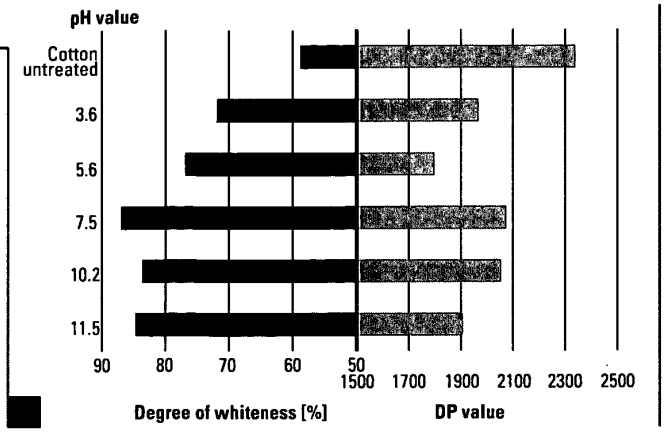



*Fig. 50*

*Dependence of pad batch bleaching on pH value*
*50°C, 2 hrs., 5.7 g/l PERACTIVE, 8.6 ml/l $H_2O_2$*

## The PERACTIVE system in impregnating bleaching

The use of the PERACTIVE system proves advantageous both for cold bleaching and also for hot bleaching. The pH value, which influences both the degree of whiteness and also the fibre damage, is of particular importance in this case.

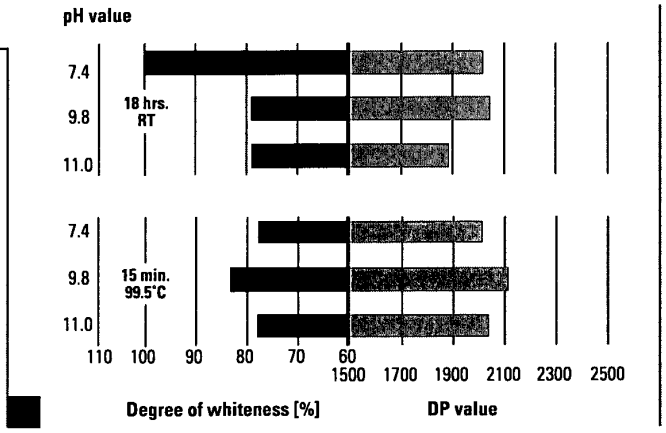



*Fig. 51*

*Influence of the pH value with impregnating bleaching*
*18 hrs. room temp. vs. 15 min./99.5°C, 1.14 g/l PERACTIVE, 1.72 ml/l $H_2O_2$*

## The PERACTIVE system in the two-stage pad steam bleaching

In the two-stage pad steam bleaching process the stage of the chlorine bleaching can be replaced without any problems by activated PERACTIVE bleaching. Advantages in regard to the fibre damage result, if peroxide bleaching is carried out first, followed by PERACTIVE bleaching.

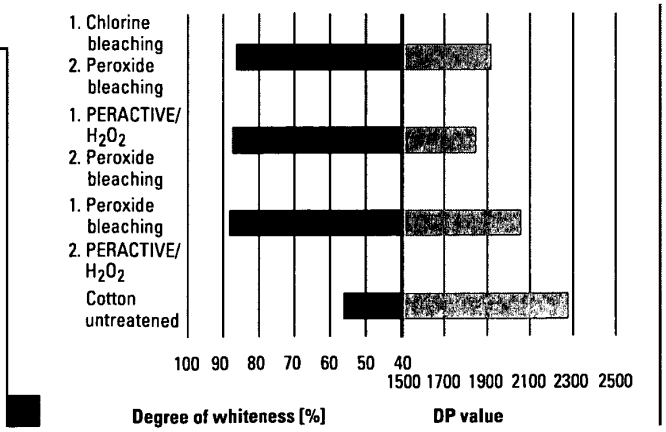



*Fig. 52*

*Two-stage pad steam bleaching process*
*Comparison of different processes*



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# PERACTIVE
## under cold wash conditions

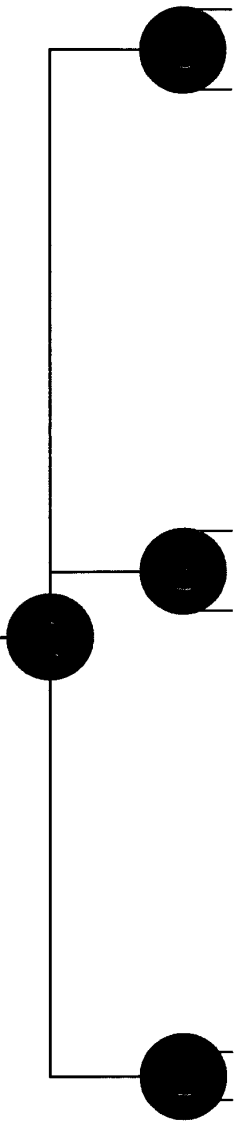
Washing processes and washing conditions differ throughout the world. Whereas washing by hand in the river with the aid of soap is common in many countries, automatic washing machines with multifunctional programs and built-in dryers are used in highly industrialized countries. Habits typical for a particular country are the temperature and length of a washing process. In many regions, such as North America and the Far East, much lower temperatures and shorter washing times are used in comparison to Europe. In order to obtain an optimum result, the laundry is often soaked over night and not washed until the next day.

The lower washing temperatures make it impossible in many countries to replace the ecologically harmful chlorine bleaching liquor by a persalt alone. The reactivity of hydrogen peroxide is not sufficiently effective under these conditions. On the other hand persalts have the advantage that they can be incorporated directly into a washing powder and the separate dosing stage can therefore be omitted. The use of a persalt activator is essential to activate the bleach. In this case PERACTIVE can be used either alone or combined with other low temperature activators.

Under cold wash conditions visible improvements in the bleaching results are possible over the whole temperature range between 10 and 40°C by using the PERACTIVE system. 4–8% PERACTIVE combined with 6–12% perborate monohydrate or percarbonate have proved effective in compact detergents, whilst 10–15% PERACTIVE are expedient in bleach boosters. The perhydrolysis of the PERACTIVE system is very fast even at 20°C, however the reactivity of the peracetic acid formed depends on the washing temperature and the reaction time. The bleaching result can be improved significantly, if PERACTIVE is already added in the soaking stage. It is able to develop its full bleaching power as a result of the length of time. Reference is made to the section on bleach boosters regarding the optimization of the bleach booster formulations.

The PERACTIVE system can be used in all powder detergents, irrespective of the type of builder system used, in bleach boosters and pre-soaking powders. Incorporation in synthetic bar soaps is possible.

PERACTIVE granules have proved successful in many countries of the world. Even under extreme climatic conditions they ensure good stability in storage and compatibility with other detergent ingredients and guarantee optimum bleaching combined with maximum sterilization.





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## Influence of concentration and temperature

The PERACTIVE system has a positive effect on the removal of stubborn stains even with short washing cycles and at low washing temperatures. Significant effects can be achieved even with bleaching agent concentrations of 0.1 g/l of a 1 : 1 mixture of PERACTIVE and PB*1 at 20°C.

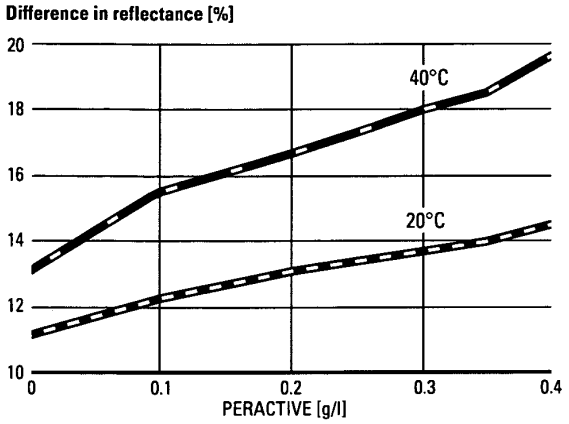



*Fig. 53*

*Dependence of the bleaching on concentration*
*2 g/l WMP (incl. bleaching system), 12 min. washing time*
*Mean value from tea and red wine stains, PERACTIVE/PB*1 – ratio 1 : 1*

## PERACTIVE suitable for cold, warm and hot washing

As a result of the incorporation of the PERACTIVE system the bleaching effect of a conventional, non-activated detergent can be visibly improved over the whole range of applications (cold, warm and hot wash), also with short washing cycles.

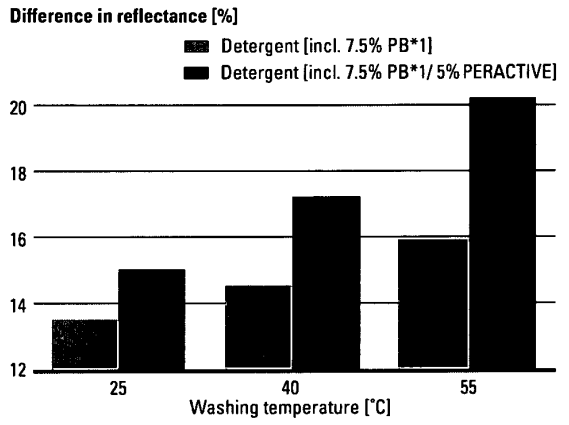



*Fig. 54*

*Dependence of the bleaching on temperature*
*2 g/l US detergent, 5.6° water hardness, 15 min.*
*Mean value from three stains*

## Effective sterilization

The antimicrobial activity of the PERACTIVE system starts even under cold wash conditions. Under these conditions perborates or hydrogen peroxide alone only display inadequate action.

| Germ | Without additive | PB*1 | PB*1/ PERACTIVE |
|---|---|---|---|
| Escherichia coli | $2.7 \times 10^6$ | $1.3 \times 10^6$ | 10 |
| Pseudomonas aeruginosa | $3.2 \times 10^6$ | $9.0 \times 10^5$ | <10 |
| Streptococcus faecalis | $1.6 \times 10^6$ | $4.2 \times 10^5$ | <10 |
| Candida albicans | $1.6 \times 10^6$ | $1.0 \times 10^5$ | 18000 |
| Staphylococcus aureus | $8 \times 10^6$ | $4.9 \times 10^6$ | <10 |

*Fig. 55*

*Sterilization in quantitative suspension test at 25°C*
*300 mg/l PB*1/ 200 mg/l PERACTIVE, 15 min.*



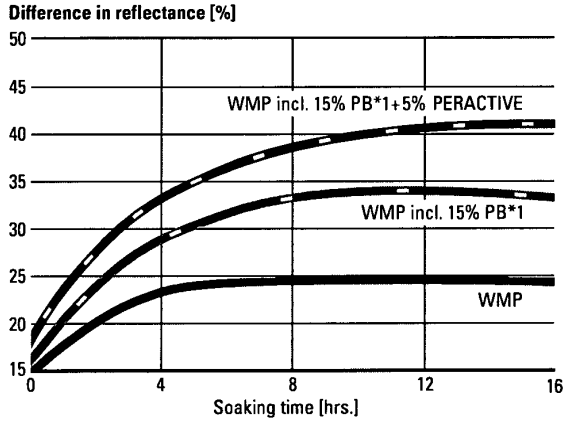
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| | Formulation 1 | Formulation 2 |
|---|---|---|
| Perborate tetrahydrate | 50 | — |
| Perborate monohydrate | — | 25 |
| PERACTIVE | 10 | 15 |
| $Na_2SO_4$ | 40 | — |
| $NaHCO_3$ | — | 50 |
| Trisodium citrate | — | 10 |

*Pre-soaking formulations* *Fig. 56*

## Better pre-soak formulations by using PERACTIVE

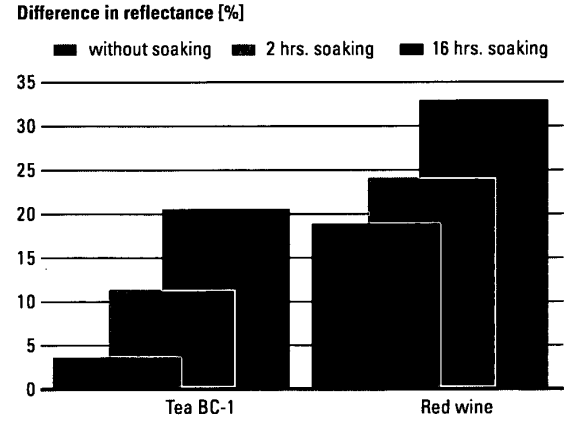
Pre-soak formulations can be formulated over wide limits. If a slow release of the peracetic acid should be obtained, the pH value should be adjusted <8. See section on bleach boosters for further information on the formulation.




*Pre-soaking tests on red wine at 20°C*
*Soaking: 2 g/l WMP*
*Subsequent washing:*
*2 g/l WMP (incl. 15% PB*1)*
*3.6° water hardness, 15 min. in LINI test*
*Fig. 57*

## Time dependence of the pre-soaking

With heavily soiled laundry it is advisable to soak the laundry to be washed in the washing machine for a time before the start of the wash. With detergents containing PERACTIVE the same degrees of whiteness can be obtained after one hour's soaking time, as after a soaking time of 12 hours when using a non-activated detergent.




*Soaking in beaker: 50% WMP=1 g/l / 40% PB*1=0.8 g/l / 10% PERACTIVE=0.2 g/l at 20°C and 5.6° water hardness.*
*Washing in LINI test: 10 min. at 20°C and 5.6° water hardness*
*Fig. 58*

## Influence of the pre-soaking on the bleaching effect

PERACTIVE displays significant effectiveness, in particular on hydrophilic stains, such as tea and red wine. Even with a cold wash, short contact times are sufficient in the soaking process to achieve significant bleaching effects.



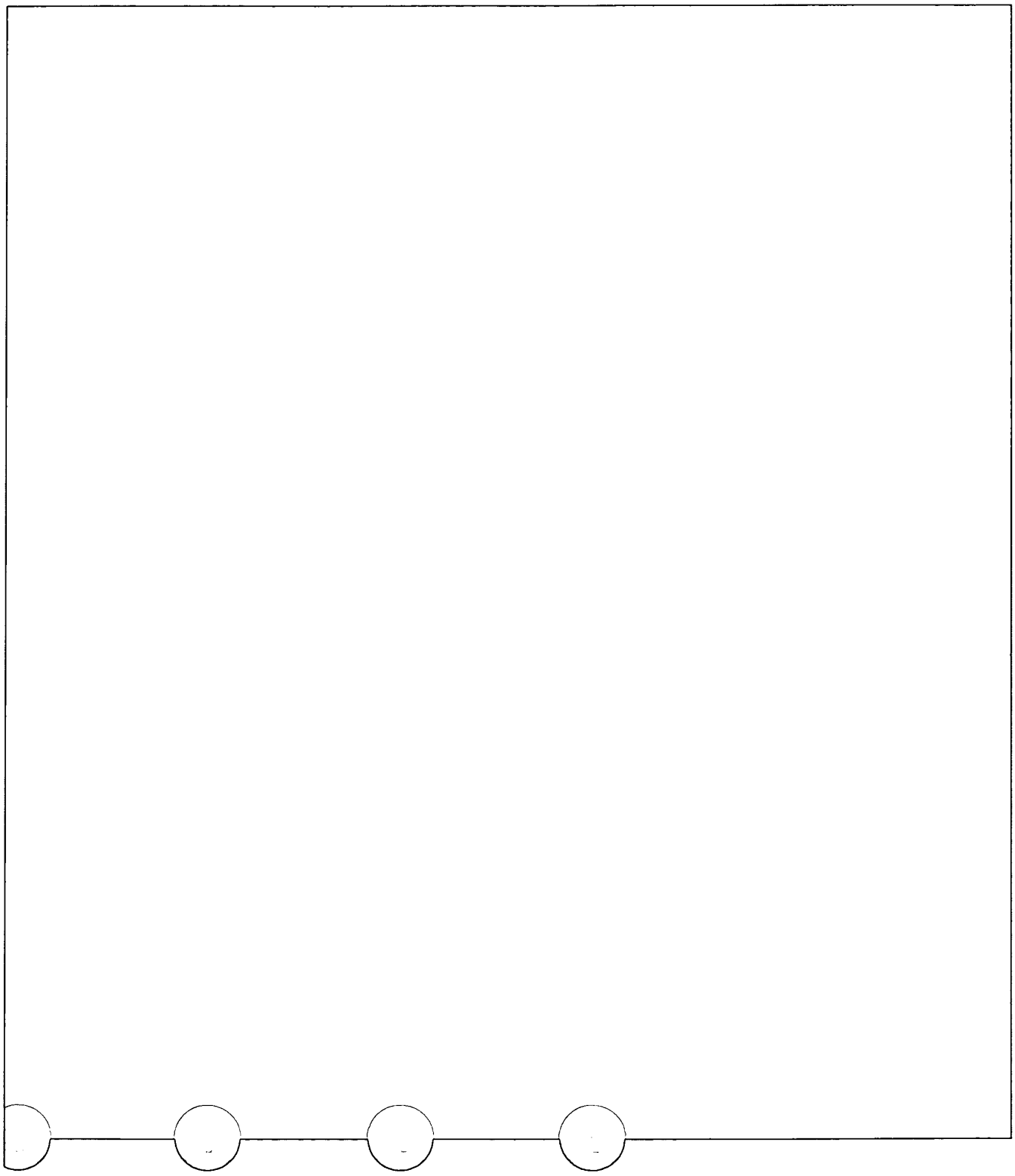
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# PERACTIVE
## in all purpose cleaners

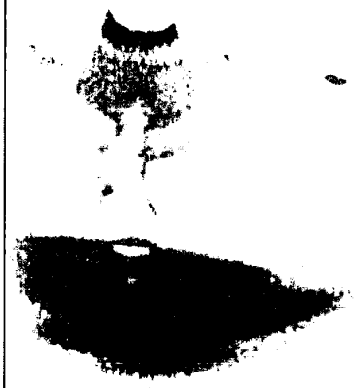
The incorporation of the PERACTIVE system in all kinds of anhydrous all-purpose cleaners in powder form does not present any problems. In this field of application in particular the antimicrobial effectiveness towards numerous germs is valued in addition to the excellent bleaching action.



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Clariant



# PERACTIVE

## Environmental aspects

# PERACTIVE –

## Production, toxicology and environmental behaviour

PERACTIVE has been produced from acetic anhydride and ethylenediamine since 1978 according to a method making economical use of resources. By recycling all the partial streams the plant guarantees integrated environmental protection and the uniformly high quality of the product with purity >99%. The continuous, computer controlled process makes the optimum use of both raw materials possible. Direct coupling products are not produced. The reaction water formed during the reaction – contaminated with traces of acetic acid – can be taken to the biological waste water treatment plant without any problems. Organic distillation residue obtained in small amounts is burned and used to produce energy.

Numerous toxicological studies and decades of consumer experience emphasize the toxicological safety of the raw material in processing and use. PERACTIVE does not have any labelling requirements.

By contrast with other detergent raw materials, such as surfactants, PERACTIVE changes during the washing process. According to the reaction mechanism it is converted into diacetylethylenediamine (DAED) with the release of peracetic acid and reaches the effluent in this form. The tests conducted on both PERACTIVE and DAED prove that the two substances are not expected to cause any harm to humans or to nature. Both are easily biodegradable, display compatibility with water organisms and were classified as harmless by the "Hauptausschuß Detergentien".

In particular when combined with sodium percarbonate PERACTIVE represents an ecologically friendly bleaching system, the constituents of which are mineralized quickly and completely. The occurrence of stable metabolites was not observed during the degradation of PERACTIVE and DAED.



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## Industrial production of PERACTIVE

PERACTIVE is produced in a two-stage process from ethylenediamine (ED) and acetic anhydride ($Ac_2O$). ED is first reacted with acetic acid (AcOH) to form diacetylethylendiamine (DAED). The reaction water formed is taken to the biological waste water treatment plant. In the second stage DAED is subsequently converted with $Ac_2O$ via the stage of triacetylethylenediamine (TriAED) into PERACTIVE. This is crystallized out of the reaction mixture, filtered, washed and dried, and if necessary also granulated.

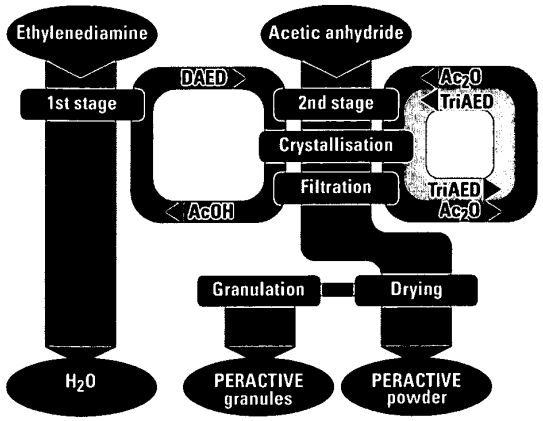



*Fig. 59* *Continuous production of PERACTIVE*

## Material flow analysis (MFA)

The MFA balances the material flow of chemical reactions. The raw materials used occur almost quantitatively in the product. Byproducts are not formed. Acetic acid formed by hydrolysis of $Ac_2O$ can be reused after internal reworking. In the case of PERACTIVE the reaction is carried out without solvents and the partial streams recycled into the relevant processes.

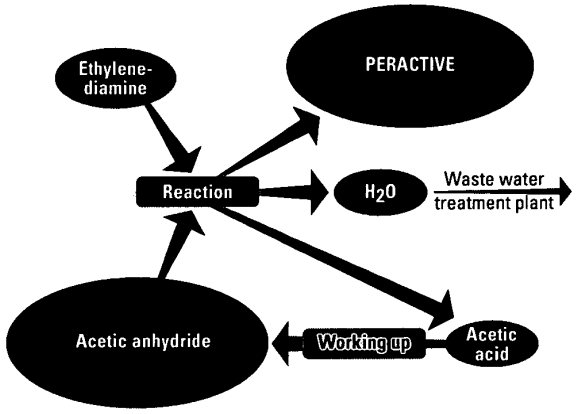



*Fig. 60* *Material flow analysis*

## Toxicological data for PERACTIVE

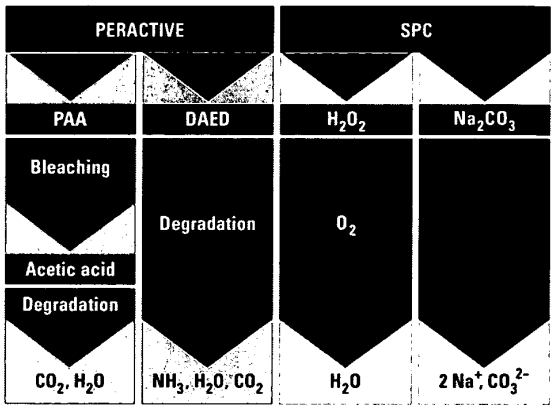
Humans come into contact with the detergent raw materials during the processing and subsequent use. Toxicological safety is therefore of utmost importance. Numerous short-term and long-term tests substantiating the safety of PERACTIVE were conducted to confirm the data. Toxicological risks emanating from PERACTIVE are not known at present. The product is not subject to compulsory labelling.

| Toxicological data | |
|---|---|
| **Acute oral toxicity** | |
| Mouse $LD_{50}$ | 5.9 g/kg body weight |
| Rat $LD_{50}$ | 10.0 g/kg body weight |
| | Almost not toxic |
| **Skin irritation** | |
| Intradermal injection (rat) | Optically not irritant |
| 3 hrs. sealed patch test (rat) | Slightly irritant |
| **Irritation of eyes** | |
| Dry powder (rat) | Slightly irritant |
| **Sensitization** | |
| Magnuson Kligman test (guineapig) | Not sensitizing |
| **Subacute oral toxicity** | |
| 13 weeks feeding study (rat) | No measurable effect |
| | 25 mg/kg body weight/day |

*Fig. 61* *Toxicological data*



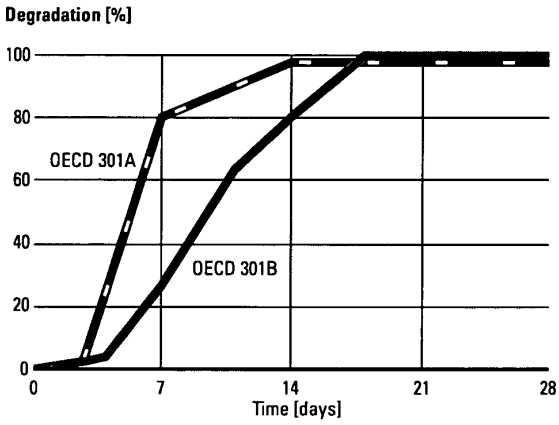
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*Mineralization of PERACTIVE/percarbonate in effluent* *Fig. 62*

## PERACTIVE/percarbonate in the environment

PERACTIVE is especially environmentally friendly when combined with percarbonate. In the washing process it is decomposed into diacetylethylenediamine (DAED) and peracetic acid (PAA), which is reduced to acetic acid. If excess peracetic acid gets into the effluent, it is decomposed catalytically by metal traces instantaneously. DAED is mineralized within a short time. Environmentally friendly percarbonate is decomposed in the washing process into sodium carbonate and hydrogen peroxide, out of which water is formed following the transfer of oxygen.




*Biodegradability of PERACTIVE in various test methods* *Fig. 63*

## Biological degradability of PERACTIVE and DAED

The biodegradability of PERACTIVE and DAED was investigated in numerous different tests. Degradation values >95% within 28 days' test duration prove their rapid degradation free of metabolites. PERACTIVE is therefore to be classified as easily biodegradable according to the OECD. The occurrence of acetylethylenediamine or free ethylenediamine as an interim stage of the degradation was ruled out by analytical methods.

**1. Biodegradability according to different methods**

| Method | Parameter | Degradation [%] |
|---|---|---|
| Closed bottle test | BSB/COD | 52–64 |
| Modified OECD screening test | DOC | 89 |
| Modified OECD screening test | TOC | 76 |
| Zahn-Wellens test | DOC | 95 |
| Sturm test | $CO_2$ | 100 |
| SCAS test | DOC | 100 |

**2. Ecotoxicological data**

| Fish toxicity | Daphnae toxicity | Algae toxicity |
|---|---|---|
| Zebrafish | $EC_{50}$ (48 hrs.) | Chlorella vulgaris |
| $LC_{50}$ (96 hrs.) > 500 mg/l | >800 mg/l | NOEC (14 days) |
| Goldfish (Carassius) | Gammarus pulex | >500 mg/l |
| $EC_{50}$ (24 hrs.) > 250 mg/l | (flea cancer) | |
| $EC_{50}$ (96 hrs.) > 1600 mg/l | $EC_{50}$ (72 hrs.) | |
| Brachydanio rerio | >800 mg/l | |
| $EC_{50}$ (96 hrs.) > 1500 mg/l | | |

*Ecotoxicological data of PERACTIVE* *Fig. 64*

## Ecotoxicological data of PERACTIVE

Both PERACTIVE and DAED must be considered for an ecological assessment. The $LC_{50}$ values towards water organisms which were observed prove that they are uncomplicated compounds with regard to acute toxicity. PERACTIVE is classified in water hazard class 0. Sequestration, heavy metal remobilization or metal fixation are not observed neither with PERACTIVE nor with DAED.



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# PERACTIVE
## Glossary

**Agglomeration**
Process to form granules

**Active oxygen**
Oxygen which is transferred in the course of the bleaching reaction from peracetic acid (by possible intermediate stages) to the substrate to be oxidized.

**Active oxygen formation**
Transfer of an oxygen atom of peracetic acid to the substrate to be bleached. The precise mechanism is not yet known.

**Anthocyanin**
Natural dye

**Builder**
Important detergent ingredient, softens the water

**Caro's acid**
Potassium peroxomonosulphate

**Catalase**
Natural enzyme, which decomposes hydrogen peroxide into oxygen and water

**Chromophoric**
Part of a molecule, which gives it colour

**Coating material**
Substances to cover other materials

**Diacyl peroxide**
Peroxide form of acetic anhydride

**Dye transfer inhibition**
Prevention of colour transfer from separated dye particles to neighbouring fabric

**Extrusion**
Process to form granules

**Flavin**
Natural dye

**Granules**
Coarse-grained solid material

**Hydrophilic soiling**
Soiling with polar groups, such as hydroxyl groups. Example: tea, red wine

**Hydrophobic soiling**
Soiling with non-polar groups, such as grass or carotene

**Hydroxyl radicals**
Reactive intermediate products with the metal catalytic decomposition of hydrogen peroxide

**Launderometer**
Laboratory washing machine

**Layered silicate**
Crystalline form of sodium disilicate, modern detergent builder and softener

**LINI test apparatus**
Laboratory washing machine

**Metabolite**
Degradation product

**Multi-chamber**
Dosing system in modern dispensing system washing machines, which enable the softener, detergent and bleach to be dosed separately

**PERACTIVE system**
Mixture of a persalt (e.g. percarbonate) with the persalt activator PERACTIVE. Peracetic acid or its salt is released from it in an aqueous alkaline medium.

**Perhydrolysis**
Reaction of PERACTIVE with hydrogen peroxide in the neutral to alkaline medium with the formation of peracetic acid

**Persalt**
Inorganic peroxide compounds such as sodium perborate or sodium percarbonate

**pH regulators**
Acid or alkaline substances, by which the pH value of the washing liquor can be modified

**Singlet oxygen**
Reactive form of natural oxygen

**Spotting**
Partial, local fading of a dye



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# PERACTIVE
## Abbreviations used

| | |
|---|---|
| **$Ac_2O$** | Acetic anhydride |
| **AcOH** | Acetic acid |
| **BC-1** | Cotton fabric with tea stain |
| **BC-3** | Cotton fabric with tea stain for low temperatures |
| **BW** | Cotton |
| **DAED** | Diacetylethylenediamine |
| **DP** | Degree of polymerization |
| **FS** | Bleach booster |
| **$H_2O_2$** | Hydrogen peroxide |
| **HDD** | Heavy duty powder detergent (heavy duty detergent) |
| **HDL** | Heavy duty liquid detergent (heavy duty liquid) |
| **IEC** | Standard detergent containing phosphate |
| **$k_1$** | Rate constant of perhydrolysis |
| **$k_2$** | Rate constant of active oxygen formation |
| **$KHSO_5$** | Potassium monoperoxosulphate |
| **LD** | Lethal dose |
| **MFA** | Material flow analysis |
| **Oa** | Active oxygen |
| **$OOH^-$** | Perhydroxyl anion |
| **P-free** | Phosphate-free |
| **PB*1** | Sodium perborate monohydrate |
| **PB*4** | Sodium perborate tetrahydrate |
| **pKa** | Negative decadic logarithm of the acid equilibrium constant |
| **RT** | Room temperature |
| **SKS-6** | Layered sodium silicate |
| **SPC** | Sodium percarbonate |
| **TAED** | Tetraacetylethylenediamine |
| **TriAED** | Triacetylethylenediamine |
| **WMP** | Phosphate-free standard detergent |



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REVIEW

# Oxygen Bleaching Systems in Domestic Laundry

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**ABSTRACT:** The oxidative bleaching process plays a key role in removing unwanted stains from laundry. This review covers methods of generation of active oxygen bleaching species, their activation and application. In addition, the requirements for commercially acceptable oxygen bleach products are discussed.

*JSD 1*, 253–261 (1998).

**KEY WORDS:** Activator, bleaching, hydrogen peroxide, laundry, oxidative, peracid, perborate, percarbonate, TAED.

Most people share a common desire to keep their clothes, bed linens, and towels clean. This desire has driven the creation of a huge detergent and white-goods industry to service it with ever-increasing sophistication. In 1996 the U.S. market for detergent products for domestic laundry was worth $4.5 billion. However efficient modern detergents and enzymes become, they still cannot remove certain stains effectively without the aid of bleaching systems. These bleaching systems are invariably oxidative in nature and are usually based on either hydrogen peroxide or hypochlorite. This article is concerned with systems that deliver bleaching using hydrogen peroxide and the various methods used to enhance their performance.

## SOURCES OF HYDROGEN PEROXIDE

Historically, sodium perborate has been the predominant source of hydrogen peroxide in laundry formulations. Sodium perborate was first produced at the turn of the century and has been used in European detergent formulations since then. In North America, where hypochlorite had been the preferred bleach, sodium perborate appeared only in the 1980s, with the advent of fast-dissolving sodium perborate monohydrate. The other principal hydrogen peroxide source is sodium percarbonate. Sodium perborate has the advantage of being inherently more stable than sodium percarbonate in that it is a true persalt, unlike sodium percarbonate which is an adduct of hydrogen peroxide and sodium carbonate. To achieve a satisfactory shelf life, sodium percarbonate requires more protection in granular form than sodium perborate. On the other hand, it has the advantage of releasing its hydrogen peroxide as fast as sodium perborate monohydrate.

Dissolved in an aqueous medium, sodium perborate is hydrolyzed producing hydrogen peroxide and sodium borate. Sodium percarbonate dissolves to release hydrogen peroxide. Since all laundry waters are basic, hydrogen peroxide dissociates to generate the perhydroxyl anion.

One possible future source of peroxide in detergent formulations could well be the use of oxidase enzymes such as glucose oxidase, which uses the glucose substrate to generate hydrogen peroxide. With the advent of routine genetic manipulation, detergent enzymes can now be engineered to be more stable and more active than their wild-type equivalents in alkaline, surfactant-laden wash waters. Patents (1,2) have already been published using this approach to generate peroxide. The advantage of this approach could be the replacement of solid peroxide sources with a substance with greater long-term stability. However, because one solid peroxide source is being replaced with the enzyme substrate, another solid, no weight or volume saving is made.

## HYDROGEN PEROXIDE IN LIQUIDS

Until recently no aqueous liquid detergent formulation on the market contained hydrogen peroxide. This situation changed in 1997 with the introduction of liquid bleach boosters containing peroxide. Stabilization of peroxide in

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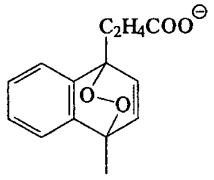
these aqueous products is achieved by an acidic pH, which is known to slow down peroxide decomposition. This pH range limits the utility of these formulations for main wash products because a large part of the cleaning action in laundry is derived from the alkalinity in the wash bath.

However, stabilization of hydrogen peroxide in alkaline detergent formulation can be achieved through careful sequestration methods and choice of surfactant and hydrotrope systems (3,4). This has now afforded the possibility of commercial liquid main wash detergent formulations containing hydrogen peroxide bleach.

## BLEACHING MECHANISM OF HYDROGEN PEROXIDE

Hydrogen peroxide decomposes to molecular oxygen and water. It has been postulated that some of this molecular oxygen is in a reactive, electronically excited state known as singlet oxygen, $^1O_2$ and that it is this singlet oxygen which is the active bleaching species. This postulate has been largely disproved by attempting to use compounds such as the endoperoxide (1; Scheme 1) as bleaching agents (5). These peroxides decompose thermally to release quantitative amounts of $^1O_2$ but do not effect bleaching of stained fabrics. The probable cause is the short lifetime of $^1O_2$, which decomposes before effective concentrations have time to reach the stain sites.

Radical species, such as perhydroxyl and hydroxyl radicals, formed during the decomposition of hydrogen peroxide have also been suggested as the bleaching species. Experiments incorporating radical trapping agents showed they have no effect on hydrogen peroxide bleaching, indicating that a radical species is not involved in bleaching (6). However, recent work (5) using different radical traps to differentiate between radical species has indicated that the conjugate base of the perhydroxyl radical $O_2^{\cdot-}$, the so-called superoxide, could be a candidate for the active oxygen species.




(1)

SCHEME 1

The generally accepted view today is that the active bleaching species is the perhydroxyl anion which acts *via* the well-known ionic mechanism of nucleophilic attack on electrophilic centers, such as alkene groups. This is illustrated by a study (6) of the reaction mechanism of perhydroxyl anion with the model stain molecules alizarin and crocetin (compounds **2** and **3**, respectively; Scheme 2).

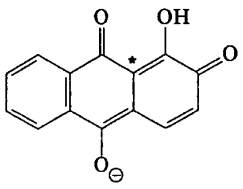
The reaction rate of alizarin bleaching was found to peak at pH 12, whereas that of crocetin increased from pH 10 and plateaued at pH 14. The increase of reaction rate at basic pH is consistent with an attack of perhydroxyl at the highlighted carbons on each molecule, aided by the electron-withdrawing effect of the carbonyls α to each double bond. In both cases, the decomposition products found were in agreement with fragmentation initiated by epoxide formation at the indicated double bond, followed by hydrolysis to a diol.

## LIMITATIONS OF HYDROGEN PEROXIDE

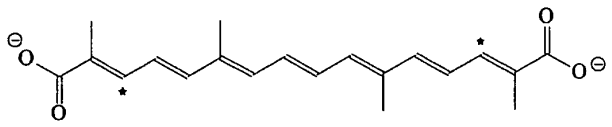
Although a cost-effective, safe and environmentally sound source of bleaching, hydrogen peroxide has one significant disadvantage for today's laundry applications: reduced efficacy at lower temperatures.

During the 1970s, the combination of the need for energy efficiency and the increased usage of synthetic fibers in Europe brought about a downward trend in wash temperatures. Instead of the traditional boil wash, washing was now commonly done at 40–60°C. Moreover, in North America domestic laundry conditions are quite unlike those in Europe. Dilutions are greater and wash temperatures are on average *ca.* 40°C. If oxygen bleach systems based on hydrogen peroxide were going to remain effective under European conditions and also challenge hypochlorite bleaches in North America, some way would have to be found to boost their performance.

In discussing efforts to boost the performance of oxygen bleaching systems, we consider first the simplest case of solution bleaching. By assuming bleach and substrate are both in solution in the absence of surfactant, second-order




(2)




(3)

SCHEME 2



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kinetics can be assumed, where the rate of bleaching is given by the equation

$$\text{rate} = k\,[\text{oxidant}]\,[\text{stain}] \quad [1]$$

and $k$ is the rate constant given by the Arrhenius equation

$$k = A \exp(-E/RT) \quad [2]$$

where $A$ is a constant, $R$ is the gas constant, $T$ is temperature and $E$ is the activation energy for the reaction. The rate equation indicates that the rate is dependent on the concentration of both the stain and the oxidant, i.e., the higher the concentration of oxidant and/or stain, the more likely two molecules will meet with the correct energy to react. Therefore, increasing dilution, as in U.S. laundry conditions, would be expected to decrease reaction rate. From the Arrhenius equation we may deduce that the reaction rate will decrease with decrease in temperature.

Constraints of price and space in the detergent formulation preclude an increase in the level of perborate or percarbonate to the extent that it would have any positive effect on bleaching performance. Increasing the washing time would also be commercially unacceptable. The only remaining option is to reduce the activation energy of the reaction, thus increasing the rate constant. This requires the use of a stronger oxidant and can be accomplished by using bleach activators and bleach catalysts.

## BLEACH ACTIVATORS

Bleach activators are essentially acylating agents and consist of an acyl moiety to which is attached a leaving group of some sort. They usually take the form of esters or imides, examples of which are tetraacetylethylenediamine (TAED) (**4**), sodium nonanoyloxybenzenesulfonate (SNOBS) (**5**), tetraacetyl glycoluril (TAGU) (**6**) and pentaacetyl glucose (PAG) (**7**) (Scheme 3). They act by acylating the perhydroxyl ion to generate peracids and peracyl anions in what is termed the perhydrolysis reaction (Scheme 4). The peracid is a more active bleaching species than hydrogen peroxide and it provides effective bleaching in the 40–60°C temperature range.

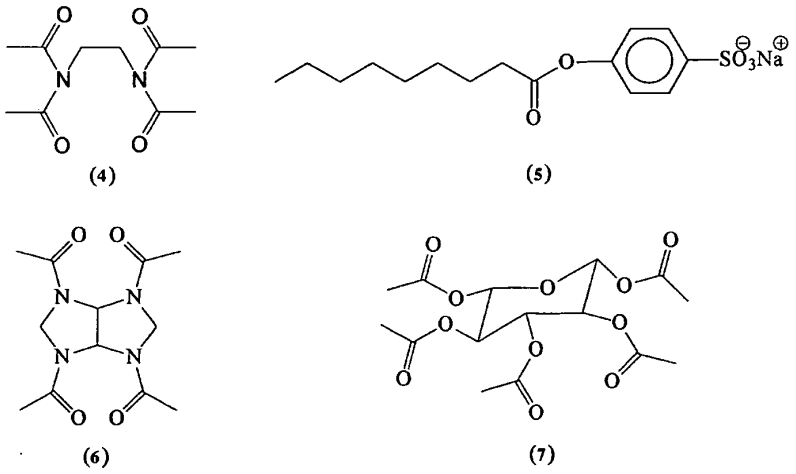
Once formed, the peracid may decompose by a number of routes (Scheme 4). The peracid may react with another molecule of activator, generating a diacyl peroxide. Diacyl peroxides have not generally been thought of as contributors to bleaching action since they break down *via* short-lived radical species. Diacyl peroxides may be perhydrolyzed back to peracids but this reaction is slower than their rate of formation and results in the decomposition of peracid.

Additionally, the peracid may hydrolyze to its carboxylic analog and may also decompose through a free radical. Hydrolysis is obviously undesirable, and free radical decomposition is not recognized as being an effective bleach mechanism. The activator may also undergo hydrolysis rather than perhydrolysis to give a carboxylic acid, again an undesirable reaction.

Therefore, an effective activator must react preferentially with perhydroxyl ion to release a stable peracid and in addition must not form significant quantities of diacyl peroxide. In this respect, TAED gives a highly favorable perhydrolysis-to-hydrolysis ratio. It has been postulated (7) that TAED forms hydrogen bonds with hydrogen peroxide during perhydrolysis, thus stabilizing the transition state and favoring perhydrolysis. Moreover, TAED does not form diacyl peroxides.

The rate of formation of peracid (PA) by perhydrolysis may be expressed by the equation

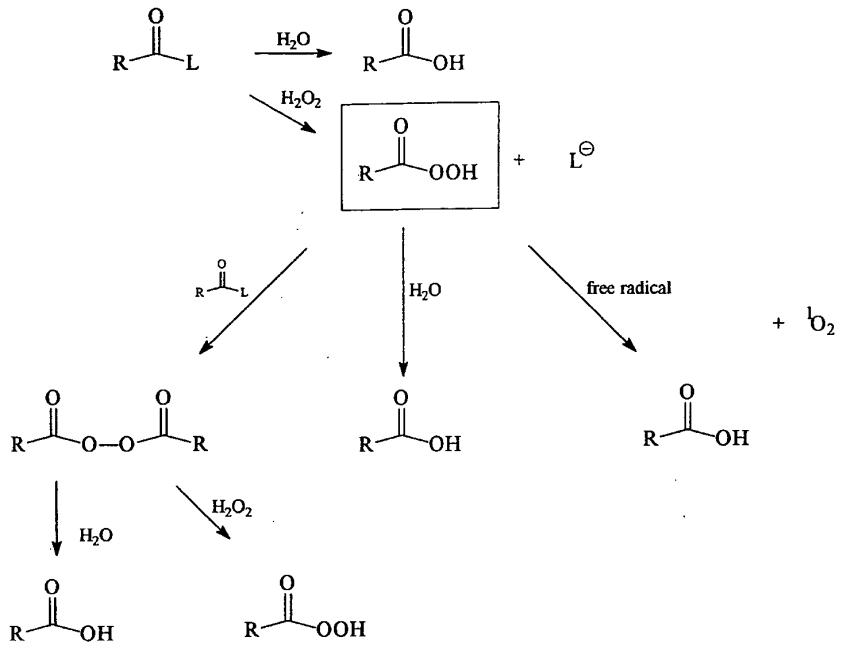
$$d[\text{PA}]/dt = k_{ph}[\text{A}][\text{H}_2\text{O}_2] - k_h[\text{A}] - k_d[\text{PA}] \quad [3]$$




SCHEME 3



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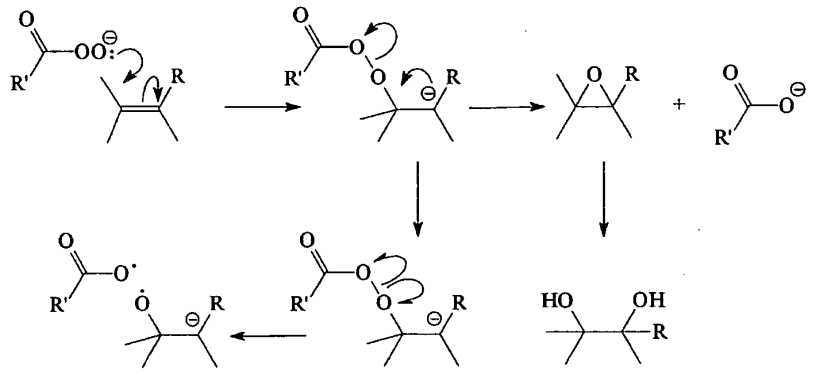
SCHEME 4

where $k_{ph}$ = perhydrolysis rate constant, $k_h$ = hydrolysis rate constant, and $k_d$ = decomposition rate constant (this has multiple components). The perhydrolysis reaction is second-order although under more concentrated European conditions, it is pseudo-first-order (8). Examination of the rate equation shows that, as with the rate of bleaching , the perhydrolysis rate will decrease with decreasing concentration and decreasing temperature. However, one favorable effect of lower wash temperatures is that the decomposition processes are slowed, leading to longer lifetime of the peracid.

## BLEACHING MECHANISMS OF BLEACH ACTIVATORS

Two mechanisms are possible for the reaction of peracid with the unsaturation of the stain chromophore. In the basic pH of the wash solution, the peracid is present in both its protonated and deprotonated form.

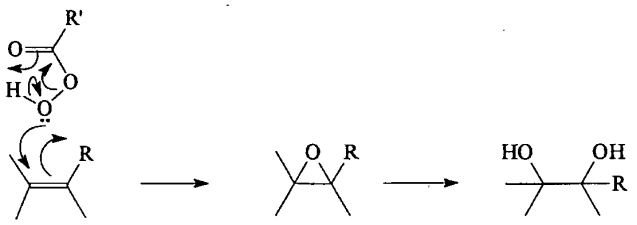
The deprotonated peracid anion reacts by nucleophilic attack as illustrated in Scheme 5. Attack of the peracid anion generates an acyl peroxide anion, which then undergoes either ring closure to form an epoxide or proton abstraction followed by homolytic cleavage to generate free-



SCHEME 5



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SCHEME 6

radical species. The epoxide will probably be hydrolyzed to a diol. In all cases the double bond is removed. This mechanism requires that R be electron-withdrawing in order to stabilize the negative charge on the carbon prior to epoxide formation. The reaction could, in theory, be insensitive to the electronegativity of the R' group. An electron-donating R' group enhances the nucleophilicity of the peracid anion but makes the acyl anion a poorer leaving group. Conversely, an electron-withdrawing R' group reduces the nucleophilicity of the peracid anion but increases the leaving propensity of the acyl anion.

Attack by the peracid itself is known as the Prilezhaev reaction and is well known in organic synthesis. It is described by Scheme 6. In this case, the alkene is nucleophilic. Electron-donating R groups increase the rate of reaction, as do electron-withdrawing R' groups on the peracid, which also increase the oxidation potential of the peracid. As in Scheme 5, the resultant epoxide may be hydrolyzed to the diol.

Whether the peracid, peracid anion, or both acid and anion together are the active bleaching species is not known. If the acid is a significant bleaching species under lower pH and the anion is the predominant bleaching species at alkaline pH, then different stains species would be expected to have different optimal pH values for bleaching, depending on the substituents on the alkene. Additionally, one stain molecule may be bleached by attack at different sites depending on pH.

Both the amount of peracid released by the activator and the nature of the peracid released by the bleach activator can affect bleaching performance. Increasing the electronegativity of the group attached to the peracid functionality increases the oxidation potential of the peracid, thus increasing its bleach performance. This may be achieved by substituting an aromatic group, as in the activator sodium benzoyloxybenzene sulfonate (**8**; Scheme 7), and is support for the participation of the peracid, as opposed to the peracid anion, in the bleach mechanism.

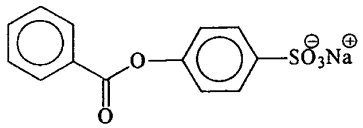
The use of activators releasing peracid with long alkyl chains, e.g., pernonanoic acid, increases the efficacy of the activator on oily stains by conferring sufficient hydrophobicity on the released peracid to partition into the oily stain. Such activators are also more effective in dilute wash baths, such as those in North America, because the peracid is surface-active which may well lead to increased local concentrations of peracid at the fiber surface (9). SNOBS (**5**) is a good example of such an activator.

## OTHER ACTIVATORS

Numerous other activators have been patented but never commercialized. Indeed, since 1967 over 700 references cite the term "bleach activator." Many of these other activators are based on acid residues other than simple aliphatic acids, presumably both to avoid prior art patents and in the hope that introducing functionality into the released peracid would somehow boost bleach performance. These include activators such as sodium nonylaminocaproylbenzenesulfonate (**9**; Scheme 8) (10) and 2-phenyl benzoxazin-4-one (**10**; Scheme 8) (11), which release peracids containing amide functions. The latter is interesting because it is neither an imide nor ester but perhydrolyzes by attack of perhydroxyl at the 4-position followed by ring opening to give a 2-substituted perbenzoic acid—a rare example where the leaving group forms part of the resultant peracid. Others include quaternary nitrogen (12,13), carbamates (14), and olefin (15) functionality as exemplified by compounds (**11**), (**12**), and (**13**), respectively. Changing the released peracid from percarboxylic to percarbonic has also been done as in compound (**14**) (16), as has the use of dibasic acids such as (**15**) (17) (for structures **11–15** see Scheme 8).

A host of different leaving groups, to release the foregoing peracids and the more common peracetic and peraliphatics, have also been claimed such as lactams (18), succinimides (19), and imidazoles (20).

As noted previously, most bleach activators release peracids. However, it is possible for the nitrile functionality to be perhydrolyzed, which leads to the formation of perimidic acids (Scheme 9). Although this short-lived species hydrolyzes rapidly, the perimidic acid can have a residence time long enough to effect bleaching (21).

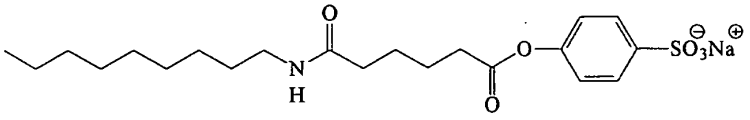


(**8**)

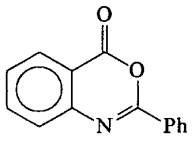
SCHEME 7



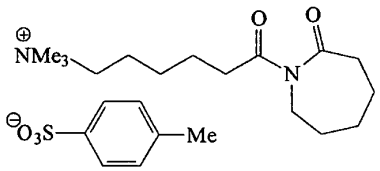
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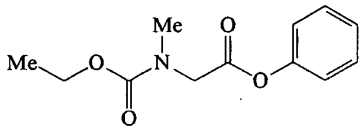
(9)



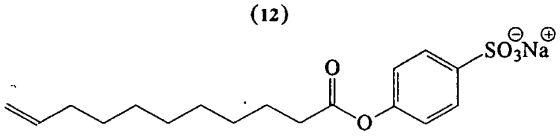
(10)



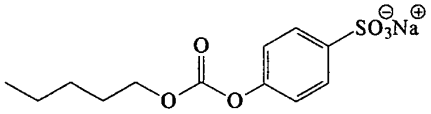
(11)



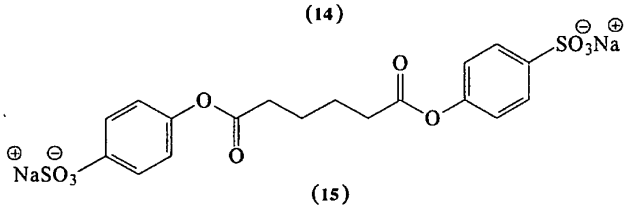
(12)



(13)

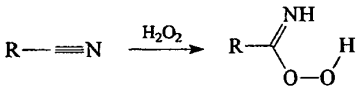


(14)



(15)

SCHEME 8



SCHEME 9

## REQUIREMENTS FOR A COMMERCIAL BLEACH ACTIVATOR

Despite the large number of bleach activators that have been patented, only two main bleach activators are currently on the world markets. The reason is that in addition to bleaching performance, a successful commercial bleach activator must satisfy a number of other criteria.

The first is cost effectiveness. The typical amount of bleach activator in a dose of activated detergent formulation is 3.6 g in the United States and 5 g in Europe, i.e., around 5% of the formulation. Therefore, any commercially viable activator must release an amount of peracid sufficient for bleaching performance within that dosage limit. This means there is a limited range of molecular weight, peracid release, and cost which must be met by a potential activator to be cost-effective relative to existing commercial



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activators, i.e., a combination of low molecular weight, high peracid release, and low manufacturing cost is needed.

The second factor is dye and fabric damage. The bleaching species that is able to differentiate between stains and fabric dyes has not been, and may never be, devised. Therefore, an extremely active bleaching species will show higher stain removal than one of lower activity but will also result in commensurately greater damage to fabric dyes and, in extreme circumstances, to the fabric itself. Again a balance must be struck, this time between stain removal and dye damage.

Finally, toxicity and environmental effects must be taken into consideration. Detergent formulations, and hence bleach activators, are used in a domestic environment. The bleach activator, along with the other ingredients in the detergent formulation, must possess sufficiently low toxicity, mutagenicity, irritancy, or sensitization to cause no ill effects at the exposure level of typical domestic use. Lack of skin sensitization potential is particularly important as, owing to the nature of the laundry process, a small amount of detergent formulation is always left on the clothes and hence in long-term contact with human skin. Bleach activators and their hydrolysis products that enter the environment with the rest of the spent detergent must have acceptably low toxicity toward aquatic organisms and be biodegradable, preferably readily biodegradable.

Given these requirements, it is not surprising that only two commercially significant bleach activators are on today's market. The dominant activator in Western Europe, also used in South America and parts of southeast Asia, is TAED. Its molecular weight is low, and it releases two molecules of peracid per molecule of activator, which makes it cost-effective. Its perhydrolysis product, peracetic acid, strikes a good balance between performance and dye damage. In addition, TAED exhibits no toxicity or skin sensitization effects, and it and its hydrolysis products are biodegradable.

Likewise, SNOBS has a similarly acceptable cost effectiveness in its home market. Although on a weight-for-weight basis, it releases about half the amount of peracid of TAED, the pernonanoic acid it releases can be more effective under dilute North American laundry conditions and stains. SNOBS has also been marketed in Japan, where washing conditions are similar to those in the United States.

Few other activators have been commercialized: PAG (**7**) and TAGU (**6**). Although PAG carries five acetyl groups, only 2.2 are released on average, which affects its cost performance adversely. TAGU yields a nonbiodegradable hydrolysis product. However, in Japan a SNOBS-type molecule, sodium lauroyloxybenzenesulfonate (SLOBS) has recently been commercialized.

## BLEACH CATALYSTS

In view of the importance of cost effectiveness, bleach catalysts offer an interesting alternative to bleach activators. Bleach activators can be thought of as oxygen transfer agents, transferring the active oxygen from peroxide to the stain *via* a peracid. Usually, no more than two molar equivalents of active oxygen can be transferred by each bleach activator molecule, which is why these activators are used at around the 5% level. A catalytic oxygen transfer agent can be expected to be effective at much lower levels and to offer potential cost performance benefits. At the same time, it would free up volume, which is particularly important in modern concentrated formulations.

Bleach catalysts are not new. Early catalysts were based on free metal ions such as Co, Mn, and Fe. However, the presence of uncomplexed metal ions usually leads to unproductive decomposition of hydrogen peroxide. Metal ions were therefore first formulated in combination with standard sequestering agents (22,23) and later complexed with ligand systems such as dipyridylamine (24). Sometimes the metals or metal complexes were supported in order to enhance stability and alleviate dye damage (25). Metal porphyrins and phthalocyanines were also patented (26,27) but not commercialized, most likely because of a combination of inadequate stability, difficult synthesis, and high cost.

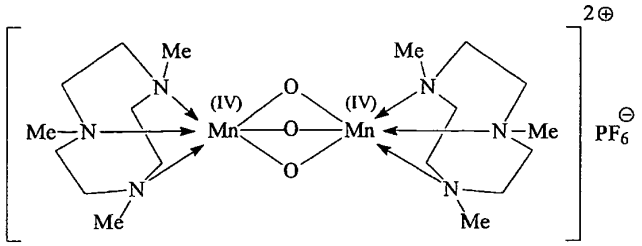
Not until 1994 was a bleach catalyst commercialized. It was a dimanganese-based complex (28) with a triazacyclononane ligand (**16**; Scheme 10) which was marketed in a European detergent formulation. Dosed at the hundredths of a percentage level, it provided effective bleaching. However, bleaching performance was accompanied by increased damage on some dyes and fabrics (29). Like peracids, bleach catalysts seemingly cannot differentiate between stain and dye. Because of fabric damage, the catalyst was withdrawn from the laundry detergent market in 1995.

This experience has not stopped research on bleach catalysts. The trend appears to be toward more complex multidentate ligands such as (**17**; Scheme 11) (30), probably with the objective of greater stabilization of the complexes to decomposition by the other wash solution ingredients and prevention of uncomplexed metal deposition on the fabric surface. Because of the extremely low dosage levels of a bleach catalyst, its manufacturing cost can be substantially higher than that of a bleach activator. In turn, this expands the scope of increasing the complexity of the catalyst molecule and permitting higher toxicity and irritancy. All the preceding place fewer constraints on the researcher searching for a commercially acceptable product.

Oxidation catalysts occur in nature in the form of oxidase and peroxidase enzymes. These are complex protein molecules with metal centers. Illustrative examples are the cytochrome peroxidase enzymes which are mainly responsible for electron transfer in primary respiration in cells. When used *in vitro*, they can catalyze the transfer of oxygen from hydrogen peroxide. They are similar to metal porphyrins, which are used by the enzyme to complex the active metal center. Enzyme systems based on peroxidase enzymes have been patented (31,32) and appear to be close

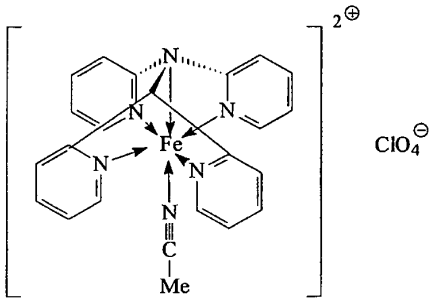


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(16)

SCHEME 10

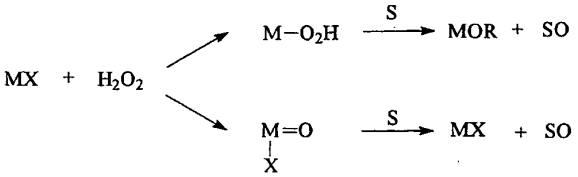


(17)

SCHEME 11

to commercialization, primarily to inhibit dye transfer in the washing solution.

Synthetically derived metal complexes or a peroxidase enzyme can effect oxidation of a substrate by three possible mechanisms. As shown in Scheme 12, the metal center may react with the peroxide to form either a peroxometal species or an oxometal species, which then reacts with the substrate. The side reaction which competes with both of these processes is free-radical decomposition of the peroxide. Early (Periodic Table) group transition metals tend to promote radical decomposition, which is generally thought to be undesirable and may explain why these metals are not commonly used as bleach catalysts. One school of thought has implicated free-radical formation in dye damage. The use of bleach catalysts with free-radical inhibitors has been claimed to reduce dye and fabric damage (33).



SCHEME 12

Bleach catalysts have obvious promise as enhancers of peroxide bleaching. Their commercial future will remain uncertain until either the problem of dye damage is solved or the laundry market becomes less sensitive to it.

## PREFORMED PERACIDS

Peracids can be delivered to a laundry solution without the use of a bleach activator. They are potentially more weight efficient than bleach activators, are immediately available for bleaching, and, in theory, require no peroxide source.

Structure/activity effects with preformed peracids are identical with those of peracids derived from bleach activators, i.e., electrophilic groups, such as perbenzoics, confer higher bleaching performance than peralkanoic acids, and substituents conferring surface activity provide greater efficacy in dilute wash solutions and on oily stains.

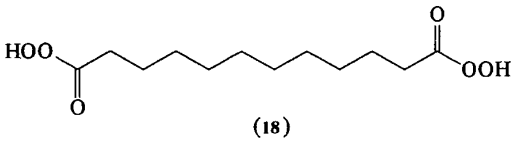
Stability is the key issue with peracids. Low-molecular-weight peracids are thermally unstable. Their concentrated solutions or solids can decompose explosively. To increase stability, a certain molecular weight is needed which, in turn, reduces the possible weight efficiency advantage over bleach activators. In addition, preformed peracids are more reactive than bleach activators toward other components in the detergent formulation and are thus less shelf-stable. Incorporation of heteroatom functionality such as amide (34) and sulfone (35) has been claimed to increase stability, as has the combination of peracid with boric acid (36). Despite a large amount of work on preformed peracids like diperoxydodecanedioic acid and peroxyphthalimidocaproic acid (**18** and **19**, respectively; see Scheme 13), the stability issues surrounding preformed peracids have mitigated against their commercialization by the detergent companies.

## THE FUTURE

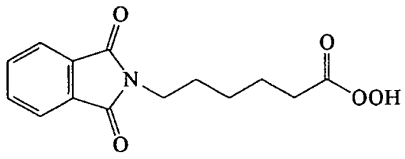
The search for bleach activators with cost-performance advantages over the currently commercialized products in Europe and North and South America will continue. New activators may be needed for emerging markets such as China or southeast Asia if the current products fail to meet the needs of these new markets.



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(18)




(19)

SCHEME 13

Microencapsulation techniques may succeed in stabilizing bleach activators in liquid detergents in the presence of hydrogen peroxide. This would make it possible to activate a heavy-duty liquid detergent and open a market segment which currently lacks a bleach system as effective as that available in powder formulations.

Bleach catalyst development will continue, probably at a greater intensity than that for bleach activators. The objective will be to exploit the potential cost-performance benefits of catalyst chemistry while attempting to reduce the dye and fabric damage problems associated with it. Enzymes may well play a significant role here, with the possibility of combining genetically engineered oxidase and peroxidase enzymes to give activated oxygen bleaching without the requirement for an oxidant.

Finally, the market awaits the holy grail of a catalyst, perhaps something like a highly active oxidase enzyme, which could catalyze the addition of atmospheric oxygen to a stain substrate and remove entirely the need for an active oxygen source in the detergent formulation. This would be the ultimate development in domestic laundry bleaching.

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IPR2025-01458 – Page 329

UNITED STATES PATENT AND TRADEMARK OFFICE

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United States Patent and Trademark Office
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www.uspto.gov

| APPLICATION NUMBER | FILING OR 371(C) DATE | FIRST NAMED APPLICANT | ATTY. DOCKET NO./TITLE |
|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 |

**CONFIRMATION NO. 2262**

Audrey A. Millemann
Weintraub Genshlea Chediak
11th Floor
400 Capitol Mall
Sacramento, CA 95814

**PUBLICATION NOTICE**

*OC000000056789313*

**Title:**Methods and compositions for the generation of peracetic acid on site at the point-of-use

**Publication No.**US-2012-0245228-A1
**Publication Date:**09/27/2012

## NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently http://pair.uspto.gov/. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

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Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

7590 11/08/2012

Audrey A. Millemann
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| EXAMINER | |
|---|---|
| SHIAO, REI TSANG | |
| ART UNIT | PAPER NUMBER |
| 1628 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 11/08/2012 | PAPER |

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

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

| Office Action Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 13/065,553 | HARVEY ET AL. | |
| | Examiner | Art Unit | |
| | REI-TSANG SHIAO | 1628 | |

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

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 1 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

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

**Status**

1)☒ Responsive to communication(s) filed on *24 March 2011*.

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

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

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

**Disposition of Claims**

5)☒ Claim(s) *1-91* is/are pending in the application.

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

6)☐ Claim(s) _____ is/are allowed.

7)☐ Claim(s) _____ is/are rejected.

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

9)☒ Claim(s) *1-91* are subject to restriction and/or election requirement.

**Application Papers**

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

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

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

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

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

**Priority under 35 U.S.C. § 119**

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

a)☐ All b)☐ Some * c)☐ None of:

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

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

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

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

**Attachment(s)**

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

## DETAILED ACTION

**1**. Claims 1-91 are pending in the application.

### *Election/Restriction*

**2.** The Markush group set forth in the claims includes both independent and distinct inventions, and patentably distinct compounds (or species) within each invention. However, this application discloses and claims a plurality of patentably distinct inventions far too numerous to list individually. Moreover, each of these inventions contains a plurality of patentably distinct compounds, also far too numerous to list individually. For these reasons provided below, restriction to one of the following Groups is required under 35 U.S.C. 121, wherein a Group is a set of patentably distinct inventions of a broad statutory category (e.g. Compounds, Methods of Use, Methods of Making, etc.):

I. Claims 1-4, drawn to products, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a liquid acetyl precursor) of the product for the search purpose.

II. Claims 5-6, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a liquid acetyl precursor) of the product for the search purpose.

III. Claims 7-25, 28-29, 32-33 and 39, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a hydrogen peroxide precursor) of the product for the search purpose.

IV. Claims 26-27, 30-31, 34-38 and 40-44, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., hydrogen peroxide-acetyl precursor) of the product for the search purpose.

V. Claims 45-48, drawn to products, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., hydrogen peroxide precursor) of the product for the search purpose.

VI. Claim 49, drawn to methods of use, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species of the product for the search purpose.

VII. Claims 50-52, drawn to products, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species of the product for the search purpose.

VIII. Claims 53-67, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a liquid acetyl precursor) of the product for the search purpose.

IX. Claims 68-76, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a liquid acetyl precursor) of the product for the search purpose.

X. Claims 77, drawn to products, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species of the product for the search purpose.

XI. Claims 78-82, drawn to products, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species of the product for the search purpose.

XII. Claims 83-91, drawn to processes of making, classified in class 514/252/206 with various subclasses. If this group is elected, applicants are requested to elect a single species (i.e., a liquid acetyl precursor) of the product for the search purpose.

In accordance with the decisions in ***In re Harnisch***, 631 F.2d 716, 206 USPQ 300 (CCPA 1980); and ***Ex parte Hozumi***, 3 USPQ2d 1059 (Bd. Pat. App. & Int. 1984), restriction of a Markush group is proper where the compounds within the group either (1) do not share a common utility, or (2) do not share a substantial structural feature disclosed as being essential to that utility. In addition, a Markush group may encompass a plurality of independent and distinct inventions where two or more members are so unrelated and diverse that a prior art reference anticipating the claim with respect to one of the members would not render the other member(s) obvious under 35 U.S.C. 103.

**Where an election of any one of Groups I-XII is made, an election of a single compound or species is further required.** Moreover**,** an election of a single compound is further required including an exact definition of each subject matter, for example, a liquid acetyl precursor or hydrogen peroxide precursor. Should applicant traverse on the ground that the compounds are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the compounds to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C 103(a) of the other.

All compounds falling outside the class(es) and subclass(es) of the selected compound and any other subclass encompassed by the election above will be directed to nonelected subject matter and will be withdrawn from consideration under 35 U.S.C. 121 and 37 C.F.R. 1.142(b). Applicant may reserve the right to file divisional

applications on the remaining subject matter. The provisions of 35 U.S.C. 121 apply with regard to double patenting covering divisional applications.

Applicant is reminded that upon cancellation of claims to a non-elected invention, the inventors must be amended in compliance with 37C.F.R. 1.48(b) if one of the currently named inventors is no longer an inventor of at least one claim remaining in the application. Any amendment of inventorship must be accompanied by a petition under 37 C.F.R. 1.48(b) and by the fee required under 37CFR 1.17(i). If desired upon election of a single compound, applicants can review the claims and disclosure to determine the scope of the invention and can **set forth** a group of compounds which are so similar within the same inventive concept and reduction to practice. Markush claims must be provided with support in the disclosure for each member of the Markush group. See MPEP 608.01(p). Applicant should exercise caution in making a selection of a single member for each substituent group on the base molecule to be consistent with the written description.

***Rationale Establishing Patentable Distinctiveness Within Each Group***

Each invention set listed above is directed to or involves the use or making of compounds which are recognized in the art as being distinct from one another because of their diverse chemical structure, their different chemical properties, modes of action, different effects and reactive conditions (MPEP 806.04, MPEP 808.01). Additionally, the level of skill in the art is not such that one invention would be obvious over either of the other inventions, i.e. they are patentable over each other. Chemical structures which are similar are presumed to function similarly, whereas chemical structures that

are not similar are not presumed to function similarly. The presumption even for similar chemical structures though is not irrebuttable, but may be overcome by scientific reasoning or evidence showing that the structure of the prior art would not have been expected to function as the structure of the claimed invention. Note that in accordance with the holdings of Application of Papesch, 50 CCPA 1084, 315 F.2d 381, 137 USPQ 43 (CCPA 1963) and In re Lalu, 223 USPQ 1257 (Fed. Cir. 1984), chemical structures are patentably distinct where the structures are either not structurally similar, or the prior art fails to suggest a function of a claimed compound would have been expected from a similar structure.

***The above Groups represent general areas wherein the inventions are independent and distinct, each from the other because of the following reasons***:

Restriction for examination purposes as indicated is proper because all these inventions listed in this action are independent or distinct for the reasons given above and there would be a serious search and examination burden if restriction were not required because one or more of the following reasons apply:

(a) the inventions have acquired a separate status in the art in view of their different classification;

(b) the inventions have acquired a separate status in the art due to their recognized divergent subject matter;

(c) the inventions require a different field of search (for example, searching different classes/subclasses or electronic resources, or employing different search queries);

(d) the prior art applicable to one invention would not likely be applicable to another invention;

(e) the inventions are likely to raise different non-prior art issues under 35 U.S.C. 101 and/or 35 U.S.C. 112, first paragraph.

**Applicant is advised that the reply to this requirement to be complete must include (i) an election of a invention to be examined** even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected invention**.

The election of an invention may be made with or without traverse. To reserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the restriction requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable on the elected invention.

If claims are added after the election, applicant must indicate which of these claims are readable upon the elected invention. Should applicant traverse on the ground that the inventions are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the inventions to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103(a) of the other invention.

### *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Rei-tsang Shiao whose telephone number is (571) 272-

0707. The examiner can normally be reached on 8:30 AM - 5:00 PM. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf, can be reached on (571)272-2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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

/REI-TSANG SHIAO/

Rei-tsang Shiao, Ph.D.
Primary Examiner, Art Unit 1628

November 02, 2012

## Search Notes

| Application/Control No. | Applicant(s)/Patent under Reexamination | |
|---|---|---|
| 13/065,553 | HARVEY ET AL. | |
| **Examiner** | **Art Unit** | |
| REI-TSANG SHIAO | 1628 | |

| SEARCHED | | | |
|---|---|---|---|
| Class | Subclass | Date | Examiner |
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| SEARCH NOTES (INCLUDING SEARCH STRATEGY) | | |
|---|---|---|
| | DATE | EXMR |
| restriction | 11/2/2012 | R.S. |
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

| | | |
|---|---|---|
| Applicants: | Michael S. Harvey, et al. | |
| Serial No.: | 13/065,553 | Art Unit: 1628<br>Examiner: Rei Tsang Shiao |
| Filing Date: | March 24, 2011 | |
| For: | Methods and Compositions for the Generation of Peracetic Acid on Site at the Point-of-Use | |

February 14, 2013
Sacramento, California 95814

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

**RESPONSE TO RESTRICTION REQUIREMENT**

Sir:

This response is submitted in reply to the Restriction Requirement mailed November 8, 2012. In response to the Examiner's requirement that applicants elect a group of claims, applicants provisionally elect Group III (Claims 7-25, 28-29, 32-33 and 39). In response to the Examiner's requirement that applicants must elect a species, applicants elect the species wherein the acetyl precursor is triacetin. In response to the Examiner's requirement that applicants identify the claims encompassing the elected species, applicants identify claim 9.

Claims 1-4 (designated Group I), Claims 5-6 (designated Group II), Claims 26-27, 30-31, 34-38 and 40-44 (designated Group IV), Claims 45-48 (designated Group V), Claim 49 (designated Group VI), Claims 50-52 (designated Group VII), Claims 53-67 (designated Group VIII), Claims 68-76 (designated Group IX), Claim 77 (designated Group X), Claims 78-82 (designated Group XI), and Claims 83-91 (designated Group



CLEAN CHEMISTRY EXHIBIT 1023
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XII) are hereby withdrawn without prejudice for presentation in one or more later co-pending divisional applications.

Respectfully submitted,

Michael S. Harvey, et al.

By: /Audrey A. Millemann/
Audrey A. Millemann (Reg. No. 44,942)
Attorney for Applicants
Weintraub Tobin Chediak Coleman Grodin Law Corporation
400 Capitol Mall, Eleventh Floor
Sacramento, California 95814
916/558-6033

# Electronic Patent Application Fee Transmittal

| | |
|---|---|
| **Application Number:** | 13065553 |
| **Filing Date:** | 24-Mar-2011 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Filer:** | Audrey A. Millemann |
| **Attorney Docket Number:** | 8568/17669 |

Filed as Small Entity

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

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Basic Filing:** | | | | |
| **Pages:** | | | | |
| **Claims:** | | | | |
| **Miscellaneous-Filing:** | | | | |
| **Petition:** | | | | |
| **Patent-Appeals-and-Interference:** | | | | |
| **Post-Allowance-and-Post-Issuance:** | | | | |
| **Extension-of-Time:** | | | | |
| Extension - 3 months with $0 paid | 2253 | 1 | 645 | 645 |

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Miscellaneous:** | | | | |
| | | | **Total in USD ($)** | **645** |

| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 14966135 |
| **Application Number:** | 13065553 |
| **International Application Number:** | |
| **Confirmation Number:** | 2262 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Correspondence Address:** | Audrey A. Millemann<br>Weintraub Genshlea Chediak<br>11th Floor<br>400 Capitol Mall<br>Sacramento CA 95814<br>US 9165586033<br>amillemann@weintraub.com |
| **Filer:** | Audrey A. Millemann |
| **Filer Authorized By:** | |
| **Attorney Docket Number:** | 8568/17669 |
| **Receipt Date:** | 14-FEB-2013 |
| **Filing Date:** | 24-MAR-2011 |
| **Time Stamp:** | 19:36:30 |
| **Application Type:** | Utility under 35 USC 111(a) |

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| | |
|---|---|
| Submitted with Payment | yes |
| Payment Type | Deposit Account |
| Payment was successfully received in RAM | $645 |

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|---|---|
| RAM confirmation Number | 7176 |
| Deposit Account | 501176 |
| Authorized User | |

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes)/ Message Digest | Multi Part /.zip | Pages (if appl.) |
|---|---|---|---|---|---|
| 1 | Response to Election / Restriction Filed | 8568_17669_ResponsetoRestriction.pdf | 66976<br>2dd726038fd9c6e10e30011614321e75fd4cf957 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 2 | Fee Worksheet (SB06) | fee-info.pdf | 29880<br>183da792facf69254d997dd57a3f32c3d5ca9139 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 96856 | | |

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

**New Applications Under 35 U.S.C. 111**

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

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

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

**New International Application Filed with the USPTO as a Receiving Office**

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

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

7590 04/01/2013

Audrey A. Millemann
Weintraub Genshlea Chediak
11th Floor
400 Capitol Mall
Sacramento, CA 95814

| EXAMINER | |
|---|---|
| SHIAO, REI TSANG | |

| ART UNIT | PAPER NUMBER |
|---|---|
| 1628 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 04/01/2013 | PAPER |

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

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

| Office Action Summary | Application No. | Applicant(s) | |
|---|---|---|---|
| | 13/065,553 | HARVEY ET AL. | |
| | Examiner | Art Unit | |
| | REI-TSANG SHIAO | 1628 | |

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

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

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

**Status**

1)☒ Responsive to communication(s) filed on *14 February 2013*.

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

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

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

**Disposition of Claims**

5)☒ Claim(s) *1-91* is/are pending in the application.

5a) Of the above claim(s) *1-6, 26-27, 30-31, 34-38, and 40-91* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *7-25,28,29,32,33 and 39* is/are rejected.

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

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

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

**Application Papers**

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

11)☒ The drawing(s) filed on *3/24/2011* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

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

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

**Priority under 35 U.S.C. § 119**

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

a)☐ All b)☐ Some * c)☐ None of:

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

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

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

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

**Attachment(s)**

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

2) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *5/10/12*.

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

4) ☐ Other: _____.

## DETAILED ACTION

**1**. Applicant's remarks filed on February 14, 2013 are acknowledged. Claims 1-91 are pending in the application.

### *Responses to Election/Restriction*

**2.** Applicant's election without arguments of Group III claim 7-25, 28-29, 32-33 and 39, in the reply filed on February 14, 2013 is acknowledged. Election of a compound triacetin of the acetyl precursor as the single species is also acknowledged. Because applicant did not distinctly and specifically point out the supposed errors in the restriction requirement, the election has been treated as an election without traverse (MPEP § 818.03(a)).

Claims 1-91 are pending in the application. The scope of the invention of the elected subject matter is as follows.

Claim 7-25, 28-29, 32-33 and 39 are drawn to processes of making, and prosecuted in the case. Claims 1-6, 26-27, 30-31, 34-38, and 40-91 are withdrawn from further consideration pursuant to 37 CFR 1.142(b), as being drawn to a nonelected invention.

The requirement is still deemed proper and therefore is made FINAL.

### *Claim Rejections - 35 USC § 112*

**3**. The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claim 7-25, 28-29, 32-33 and 39 are rejected under 35 U.S.C. 112, first paragraph, because the specification, while being enabling for the acetyl precursor represents triacetin, does not reasonably provide enablement for the acetyl precursor without limitation, see claim 7. The specification does not enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make the invention commensurate in scope with these claims. Dependent claims 8-25, 28-29, 32-33 and 39 are also rejected along with claim 7 under 35 U.S.C. 112, first paragraph.

In *In re Wands*, 8 USPQ2d 1400 (1988), factors to be considered in determining whether a disclosure meets the enablement requirement of 35 U.S.C. 112, first paragraph, have been described. They are:

1. the nature of the invention,
2. the state of the prior art,
3. the predictability or lack thereof in the art,
4. the amount of direction or guidance present,
5. the presence or absence of working examples,
6. the breadth of the claims,
7. the quantity of experimentation needed, and
8. the level of the skill in the art.

In the instant case:

**The nature of the invention**

The nature of the invention of claims 7-25, 28-29, 32-33 and 39 is drawn to processes of making peracetic acid solution, wherein the acetyl precursor is without limitation (i.e., no named compounds), see claim 7.

**The state of the prior art and the predictability or lack thereof in the art**

The state of the prior art is DiCosimo et al. US 2007/0082832. DiCosimo et al. '832 discloses a similar process for preparing peracetic acid solution, see column 27.

**The amount of direction or guidance present and the presence or absence of working examples**

The only direction or guidance present in the instant specification is the acetyl precursor representing triacetin, see pages 9-10 of the specification. There are no working examples present for "acetyl precursor" without limitation (i.e., no named compounds)" of the instant invention found in the specification.

**The breadth of the claims**

The breadth of the claims is the instant processes comprising any "acetyl precursor" without limitation (i.e., no named compounds).

**The quantity of experimentation needed**

The quantity of experimentation needed is undue experimentation. One of skill in the art would need to determine what “acetyl precursor” without limitation (i.e., no named compounds) would be used by the instant invention, if any.

**The level of the skill in the art**

The level of skill in the art is high. However, due to the unpredictability in the pharmaceutical art, it is noted that each embodiment of the invention is required to be individually assessed for physical characteristics to determine which acetyl precursor are used. Thus, the specification fails to provide sufficient support of the broad scope of the compounds of the instant claims for the “acetyl precursor”.

As a result necessitating one of skill to perform an exhaustive search for which “acetyl precursor”, can be prepared of the instant claims in order to practice the claimed invention. Thus, factors such as "sufficient working examples", "the level of skill in the art" and "predictability", etc. have been demonstrated to be sufficiently lacking in the instantly claimed compounds. In view of the breadth of the claim, the chemical nature of the invention, and the lack of working examples regarding the activity of the claimed “acetyl precursor” without limitation, one having ordinary skill in the art would have to undergo an undue amount of experimentation to use the invention commensurate in scope with the claims.

Genentech Inc. v. Novo Nordisk A/S (CA FC) 42 USPQ2d 1001, states that “ a patent is not a hunting license. It is not a reward for search, but compensation for its successful conclusion" and "patent protection is granted in return for an enabling

disclosure of an invention, not for vague intimations of general ideas that may or may not be workable".

Therefore, in view of the Wands factors and *In re Fisher* (CCPA 1970) discussed above, to practice the claimed invention herein, a person of skill in the art would have to engage in undue experimentation, with no assurance of success. This rejection can be overcome by incorporation of the limitation “acetyl precursor” into claim 7 (i.e., see claim 9) respectively would obviate the rejection.

**4**. The following is a quotation of the second paragraph of 35 U.S.C. 112:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 7-25, 28-29, 32-33 and 39 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Claim 7 recites the limitation “acetyl precursor” without named specific compounds is indefinite and ambiguous, i.e., see line 3. It is unclear what the scope of “acetyl precursor” is. The “acetyl precursor” is from any organic compounds having multiple functionality. Such breath in view of the limited exemplification and the lack of scope of subject matter resulted from a search of the prior art indicated that the “scope” of claim 7 cannot be ascertained. In view of the high degree of unpredictability of the chemical art and “acetyl precursor” must be made available at the time the invention was made, i.e., filing of application, the broad scope cannot be supplemented with future discovery of new “acetyl precursor”. It is recommended that “acetyl precursor” be limited to the specific disclosure in the specification, i.e., triacetin of claim 9. Dependent

claims 8-25, 28-29, 32-33 and 39 are also rejected along with claim 7 under 35 U.S.C. 112, second paragraph.

***Conclusion***

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Rei-tsang Shiao whose telephone number is (571) 272-0707. The examiner can normally be reached on 8:30 AM - 5:00 PM. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf, can be reached on (571)272-2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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

/REI-TSANG SHIAO/

Rei-tsang Shiao, Ph.D.
Primary Examiner, Art Unit 1628

March 14, 2013

| Notice of References Cited | Application/Control No. 13/065,553 | Applicant(s)/Patent Under Reexamination HARVEY ET AL. | |
|---|---|---|---|
| | Examiner REI-TSANG SHIAO | Art Unit 1628 | Page 1 of 1 |

**U.S. PATENT DOCUMENTS**

| * | | Document Number Country Code-Number-Kind Code | Date MM-YYYY | Name | Classification |
|---|---|---|---|---|---|
| * | A | US-2007/0082832 | 04-2007 | DiCosimo et al. | 510/305 |
| | B | US- | | | |
| | C | US- | | | |
| | D | US- | | | |
| | E | US- | | | |
| | F | US- | | | |
| | G | US- | | | |
| | H | US- | | | |
| | I | US- | | | |
| | J | US- | | | |
| | K | US- | | | |
| | L | US- | | | |
| | M | US- | | | |

**FOREIGN PATENT DOCUMENTS**

| * | | Document Number Country Code-Number-Kind Code | Date MM-YYYY | Country | Name | Classification |
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**NON-PATENT DOCUMENTS**

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

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

## Search Notes

| Application/Control No. | Applicant(s)/Patent under Reexamination | |
|---|---|---|
| 13/065,553 | HARVEY ET AL. | |
| **Examiner** | **Art Unit** | |
| REI-TSANG SHIAO | 1628 | |

| SEARCHED | | | |
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| Class | Subclass | Date | Examiner |
| 514 | 557 | 3/14/2013 | R.S. |
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| SEARCH NOTES (INCLUDING SEARCH STRATEGY) | | |
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| | DATE | EXMR |
| STN, structure, inventor names | 3/4/2013 | R.S. |
| EAST class/subclass | 3/14/2013 | R.S. |
| PALM inventor names | 3/14/2013 | R.S. |
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Exp. Mail EM 653467405 US

PTO/SB/08a (07-09)
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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 2

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1764 |
| Examiner Name | |
| Attorney Docket Number | 8568/17769 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
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| | | US- | | | |

**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3]-Number[4]-Kind Code[5] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
|---|---|---|---|---|---|---|
| | 1 | EP 0 563 460 B1 | 07-01-1998 | The Procter & Gamble Co. | | |
| | 2 | WO 01/46519 A1 | 06-28-2001 | Warwick International | | |
| | 3 | WO 2008/140988 A1 | 11-20-2008 | Danisco US Inc. | | |
| | 4 | WO 2010/005607 A2 | 01-14-2010 | Electron Research & Dev. | | |
| | | | | | | |
| | | | | | | |

| Examiner Signature | | Date Considered | |
|---|---|---|---|

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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Sheet 2 of 2

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | ~~4761~~ 1628 |
| Examiner Name | R.T. Shiao |
| Attorney Docket Number | 8568/17669 |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | T[2] |
|---|---|---|---|
| | 1 | LEVENEUR, et al., "Interaction of Instrinsic Kinetics and Internal Mass...Acids," Chemical Engineering Science 64 (2009) pp.4101-4114 | |
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| Examiner Signature | /Rei Tsang Shiao/ | Date Considered | 3/14/2013 |
|---|---|---|---|

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

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ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /R.S./

**EAST Search History**

**EAST Search History (Prior Art)**

| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
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| L6 | 3193 | (514/557).CCLS. | US-PGPUB; USPAT; USOCR | OR | OFF | 2013/03/14 15:54 |

**EAST Search History (Interference)**

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# BIB DATA SHEET

**CONFIRMATION NO. 2262**

| SERIAL NUMBER | FILING or 371(c) DATE | CLASS | GROUP ART UNIT | ATTORNEY DOCKET NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011<br>RULE | 514 | 1628 | 8568/17669 |

**APPLICANTS**

Michael S. Harvey, Modesto, CA;
Jonathan N. Howarth, Modesto, CA;

** CONTINUING DATA **********

** FOREIGN APPLICATIONS **********

** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** ** SMALL ENTITY **
04/08/2011

| Foreign Priority claimed ☐ Yes ☑ No<br>35 USC 119(a-d) conditions met ☐ Yes ☑ No<br>Verified and Acknowledged /REI-TSANG SHIAO/ Examiner's Signature | ☐ Met after Allowance<br>R.S. Initials | STATE OR COUNTRY | SHEETS DRAWINGS | TOTAL CLAIMS | INDEPENDENT CLAIMS |
|---|---|---|---|---|---|
| | | CA | 1 | 91 | 11 |

**ADDRESS**

Audrey A. Millemann
Weintraub Genshlea Chediak
11th Floor
400 Capitol Mall
Sacramento, CA 95814
UNITED STATES

**TITLE**

Methods and compositions for the generation of peracetic acid on site at the point-of-use

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| 3271 | FEES: Authority has been given in Paper<br>No._____ to charge/credit DEPOSIT ACCOUNT<br>No._____ for following: | ☐ All Fees<br>☐ 1.16 Fees (Filing)<br>☐ 1.17 Fees (Processing Ext. of time)<br>☐ 1.18 Fees (Issue)<br>☐ Other _____<br>☐ Credit |

## Index of Claims

| Application/Control No. | Applicant(s)/Patent under Reexamination |
|---|---|
| 13/065,553 | HARVEY ET AL. |
| **Examiner** | **Art Unit** |
| REI-TSANG SHIAO | 1628 |

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| √ | Rejected | – | (Through numeral) Cancelled | N | Non-Elected | A | Appeal |
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| Claim | | Date | | | | | | | | |
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| Final | Original | 3/14/13 | | | | | | | | |
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

| | | |
|---|---|---|
| Applicants: Michael S. Harvey, et al. | ) | |
| | ) | |
| Serial No.: 13/065,553 | ) | Art Unit: 1628 |
| | ) | Examiner: Rei Tsang Shiao |
| Filing Date: March 24, 2011 | ) | |
| | ) | |
| For: Methods and Compositions for the Generation of Peracetic Acid on Site at the Point-of-Use | ) | |

May 23, 2013
Sacramento, California 95814

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

**AMENDMENT**

This amendment is submitted in response to the non-final office action mailed on April 1, 2013.

Amendments to the claims begin on page 2 of this paper.

Remarks/Arguments begin on page 18 of this paper.



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## Amendments to the Claims

This listing of claims will replace all prior versions and listings of claims in the application.

## Listing of Claims

1. (withdrawn) - A hydrogen peroxide-acetyl precursor solution, comprising:

    a. aqueous hydrogen peroxide;

    b. a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide;

    c. a trace amount of peracetic acid; and

    d. water.

2. (withdrawn) - The solution of claim 1, wherein said liquid acetyl precursor is triacetin.

3. (withdrawn) - The solution of claim 2, wherein said aqueous hydrogen peroxide is about 23% to about 40% and said triacetin is about 20% to about 53%, and further wherein the mole ratio of said hydrogen peroxide to said triacetin is about 2.98:1 to about 12.84:1.

4. (withdrawn) - The solution of claim 3, wherein said aqueous hydrogen peroxide is about 27% and said triacetin is about 46%, and further wherein said mole ratio of said hydrogen peroxide to said triacetin is about 3.8:1.

5. (withdrawn) - A method of preparing a hydrogen peroxide-acetyl precursor solution, comprising:

    a. introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and



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b. allowing the liquid acetyl precursor and the solution of aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

6. (withdrawn) - The composition of claim 5, wherein the liquid acetyl precursor is triacetin.

7. (Currently amended) A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing a hydrogen peroxide-triacetin ~~acetyl precursor~~ solution to the water;

c. mixing the hydrogen peroxide-triacetin ~~acetyl precursor~~ solution and 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.

8. (Currently amended) The method of claim 7, further comprising, prior to step (b), a step of providing the hydrogen peroxide-triacetin ~~acetyl precursor~~ solution comprising: introducing triacetin ~~a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide~~ to a solution of aqueous hydrogen peroxide; and allowing the triacetin ~~liquid acetyl precursor~~ and the solution of aqueous hydrogen peroxide to mix to form the hydrogen peroxide-triacetin ~~acetyl precursor~~ solution.



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9. (Cancelled)

10. (original) - The method of claim 9, wherein the hydrogen peroxide-triacetin solution has a mole ratio of hydrogen peroxide to triacetin of about 2.98:1 to about 12.84:1.

11. (original) - The method of claim 7, wherein the provided water is an aqueous stream.

12. (original) - The method of claim 7, wherein the provided water is contained in a mixing tank or other vessel.

13. (original) - The method of claim 9, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

14. (original) - The method of claim 13, wherein the sodium hydroxide is about 1.82% to about 7.28%.

15. (original) - The method of claim 7, wherein step (d) is performed simultaneously with step (b).

16. (original) - The method of claim 7, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.



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17. (original) - The method of claim 16, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

18. (original) - The method of claim 17, further comprising, after step (e), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

19. (original) - The method of claim 16, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

20. (original) - The method of claim 14, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

21. (original) - The method of claim 7, wherein steps (a) through (e) are performed on a continuous basis.

22. (original) - The method of claim 7, wherein steps (a) through (e) are performed on an intermittent basis.

23. (original) - The method of claim 7, wherein the peracetic acid solution is for immediate use.



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24. (original) - The method of claim 7, further comprising, after step (e), a step of adding a source of acid to stabilize the non-equilibrium solution of peracetic acid for storing and using throughout a working day.

25. (original) - The method of claim 7, wherein the peracetic acid solution is prepared on a site having a point-of-use.

26. (withdrawn) - A method of generating a non-equilibrium solution of peracetic acid for use on a site having a point-of-use of peracetic acid, comprising:

a. providing water on a site;

b. providing a hydrogen peroxide-acetyl precursor solution on the site having a point-of-use;

c. introducing the hydrogen peroxide-acetyl precursor solution to the water;

d. mixing the hydrogen peroxide-acetyl precursor solution and the water to form a mixture;

e. providing an aqueous source of an alkali metal or earth alkali metal hydroxide on the site having the point-of-use;

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

g. forming a reaction medium comprising a non-equilibrium solution of peracetic acid for use at the point-of-use of peracetic acid.

27. (withdrawn) - The method of claim 26, further comprising, prior to step (b), a step of providing the hydrogen peroxide-acetyl precursor solution comprising: introducing a liquid

acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide; and allowing the liquid acetyl precursor and the solution of aqueous hydrogen peroxide to mix to form the hydrogen peroxide-acetyl precursor solution.

28. (original) - The method of claim 8, wherein the liquid acetyl precursor is triacetin defining a hydrogen peroxide-triacetin solution.

29. (original) - The method of claim 28, wherein the hydrogen peroxide-triacetin solution has a mole ratio of hydrogen peroxide to triacetin of about 2.98:1 to about 12.84:1.

30. (withdrawn) - The method of claim 26, wherein the provided water is an aqueous stream.

31. (withdrawn) - The method of claim 26, wherein the provided water is contained in a mixing tank or other vessel.

32. (original) - The method of claim 28, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

33. (original) - The method of claim 32, wherein the sodium hydroxide is about 1.82% to about 7.28%.

34. (withdrawn) - The method of claim 26, wherein step (d) is performed simultaneously with step (b).



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35. (withdrawn) - The method of claim 26, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

36. (withdrawn) - The method of claim 35, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

37. (withdrawn) - The method of claim 36, further comprising, after step (e), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

38. (withdrawn) - The method of claim 35, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

39. (original) - The method of claim 33, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

40. (withdrawn) - The method of claim 26, wherein steps (a) through (e) are performed on a continuous basis.

41. (withdrawn) - The method of claim 26, wherein steps (a) through (e) are performed on an intermittent basis.



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42. (withdrawn) - The method of claim 26, wherein the peracetic acid solution is for immediate use.

43. (withdrawn) - The method of claim 26, further comprising, after step (e), a step of adding a source of acid to stabilize the non-equilibrium solution of peracetic acid for storing and using throughout a working day.

44. (withdrawn) - The method of claim 26, wherein the peracetic acid solution is prepared on a site having a point-of-use.

45. (withdrawn) - A non-equilibrium solution of peracetic acid made by the method of claim 7 for use as a disinfectant or sanitizer.

46. (withdrawn) - The solution of claim 45 for clean-in-place pipeline and equipment cleaning.

47. (withdrawn) - The solution of claim 45 for use in washing fruits and vegetables.

48. (withdrawn) - The solution of claim 45 for use in the treatment of meat, poultry, and seafood.

49. (withdrawn) - A method for sanitizing a surface, which comprises generating a non-equilibrium solution of peracetic acid comprising:



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peracetic acid, hydrogen peroxide, triacetin, 1,2,3-propanetriol, a source of an alkali metal or earth alkali metal hydroxide, and water.

50. (withdrawn) - A non-equilibrium solution of peracetic acid, comprising:

a. peracetic acid;

b. hydrogen peroxide;

c. triacetin;

d. 1,2,3-propanetriol;

e. an aqueous source of an alkali metal or earth alkali metal hydroxide; and

f. water.

51. (withdrawn) - The solution of claim 50, wherein said solution has a pH of about 11.2 to about 13.37.

52. (withdrawn) - The solution of claim 50, wherein said peracetic acid is about 1% to about 7.1%.

53. (withdrawn) - A method of generating a non-equilibrium solution of peracetic acid, comprising:

a. providing water;

b. introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide and aqueous hydrogen peroxide to the water;

c. mixing the liquid acetyl precursor and the aqueous hydrogen peroxide with the water to form a mixture;



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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.

54. (withdrawn) - The method of claim 53, wherein the liquid acetyl precursor is triacetin defining a hydrogen peroxide-triacetin solution.

55. (withdrawn) - The method of claim 53, wherein the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced simultaneously.

56. (withdrawn) - The method of claim 53, wherein the liquid acetyl precursor and the aqueous hydrogen peroxide are introduced sequentially with either one first.

57. (withdrawn) - The method of claim 53, wherein the provided water is an aqueous stream.

58. (withdrawn) - The method of claim 53, wherein the provided water is contained in a mixing tank or other vessel.

59. (withdrawn) - The method of claim 54, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

60. (withdrawn) - The method of claim 59, wherein the sodium hydroxide is about 1.82% to about 7.28%.



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61. (withdrawn) - The method of claim 53, wherein step (d) is performed simultaneously with step (b).

62. (withdrawn) - The method of claim 53, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

63. (withdrawn) - The method of claim 62, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

64. (withdrawn) - The method of claim 63, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

65. (withdrawn) - The method of claim 60, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

66. (withdrawn) - The method of claim 53, wherein said steps (a) through (e) are performed on a continuous basis.

67. (withdrawn) - The method of claim 53, wherein said steps (a) through (e) are performed on an intermittent basis.



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68. (withdrawn) - A method of generating a non-equilibrium solution of peracetic acid on a site having a point-of-use, comprising:

a. providing water on a site;

b. providing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide and aqueous hydrogen peroxide on the site having a point-of-use;

c. introducing the liquid acetyl precursor and the aqueous hydrogen peroxide to the water;

d. mixing the aqueous hydrogen peroxide and the liquid acetyl precursor with the water to form a mixture;

e. providing an aqueous source of an alkali metal or earth alkali metal hydroxide water on the site having the point-of-use;

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

g. forming a reaction medium comprising a non-equilibrium solution of peracetic acid for use at the point-of-use.

69. (withdrawn) - The method of claim 68, wherein the liquid acetyl precursor is triacetin.

70. (withdrawn) - The method of claim 68, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

71. (withdrawn) - The method of claim 70, wherein the sodium hydroxide is about 1.82% to about 7.28%.

72. (withdrawn) - The method of claim 68, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid.

73. (withdrawn) - The method of claim 72, wherein the time to maximize the conversion of the hydrogen peroxide and the acetyl precursor into peracetic acid is about 30 seconds to about five minutes.

74. (withdrawn) - The method of claim 68, further comprising, after step (g), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide and acetyl precursor that are converted into peracetic acid.

75. (withdrawn) - The method of claim 72, wherein the acetyl precursor is triacetin and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

76. (withdrawn) - The method of claim 71, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

77. (withdrawn) - An on site non-equilibrium peracetic acid generation system, comprising:

a first container comprising a first solution wherein said first solution comprises:

aqueous hydrogen peroxide;

a liquid acetyl precursor that is soluble in said aqueous hydrogen peroxide;

a trace amount of peracetic acid; and

water;



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a second container comprising a second solution wherein said second solution comprises:

an aqueous source of an alkali metal or earth alkali metal hydroxide; and

means for mixing the first solution, water, and the second solution to generate a non-equilibrium peracetic acid solution.

78. (withdrawn) - A freely-flowable solid composition, comprising:

a. a liquid acetyl precursor;

b. a water-soluble solid source of hydrogen peroxide; and

c. a water-soluble solid source of alkalinity.

79. (withdrawn) - The composition of claim 78, wherein said liquid acetyl precursor is triacetin.

80. (withdrawn) - The composition of claim 79, wherein said triacetin is about 0.99% to about 8.45%.

81. (withdrawn) - The composition of claim 78, wherein said solid source of hydrogen peroxide is sodium percarbonate and is about 13% to about 54% of the total.

82. (withdrawn) - The composition of claim 78, wherein said solid source of alkalinity is about 24% to about 44% of the total.



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83. (withdrawn) - A method of making a solid composition for bleaching and stain removal, comprising:

forming a homogenous freely-flowable solid by blending a liquid acetyl precursor, a water-soluble solid source of hydrogen peroxide, and a water-soluble solid source of alkalinity.

84. (withdrawn) - The method of claim 83, wherein the liquid acetyl precursor is triacetin.

85. (withdrawn) - The method of claim 84, wherein the triacetin is about 0.99% to about 8.45%.

86. (withdrawn) - The method of claim 83, wherein the solid source of hydrogen peroxide is about 13% to about 54%.

87. (withdrawn) - The composition of claim 83, wherein the solid source of alkalinity is about 24% to about 44% of the total.

88. (withdrawn) - The method of claim 83, further comprising adding a metal chelating agent.

89. (withdrawn) - The method of claim 83, further comprising adding a surfactant.

90. (withdrawn) - The method of claim 83, further comprising adding a compound to sequester water hardness.



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91. (withdrawn) - The method of claim 83, further comprising adding an inert solid filler.



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## Remarks/Arguments

Applicants respectfully traverse the rejections in the Office Action and request reconsideration.

### I. Rejection Under 35 U.S.C. Section 112, First and Second Paragraphs

The Examiner has rejected claims 7-25, 28-29, 32, 33, and 39 under 35 U.S.C. section 112, first and second paragraphs, as not enabled and indefinite, respectively, in the use of the phrase "acetyl precursor." The Examiner has suggested that Applicants amend independent claim 7 to replace "acetyl precursor" with "triacetin" as claimed in dependent claim 9.

Applicants appreciate the Examiner's suggestion and have amended claim 7, as well as dependent claim 8, to replace "acetyl precursor" with "triacetin." Applicants have cancelled claim 9. Thus, all of the claims under examination include the limitation of triacetin. Applicants request that the rejections under section 112 be withdrawn.

Date: May 23, 2013

Respectfully submitted,

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# Electronic Patent Application Fee Transmittal

| | |
|---|---|
| **Application Number:** | 13065553 |
| **Filing Date:** | 24-Mar-2011 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Filer:** | Audrey A. Millemann/Alma Martinez |
| **Attorney Docket Number:** | 8568/17669 |

Filed as Small Entity

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

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Basic Filing:** | | | | |
| **Pages:** | | | | |
| **Claims:** | | | | |
| **Miscellaneous-Filing:** | | | | |
| **Petition:** | | | | |
| **Patent-Appeals-and-Interference:** | | | | |
| **Post-Allowance-and-Post-Issuance:** | | | | |
| **Extension-of-Time:** | | | | |

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Miscellaneous:** | | | | |
| Submission- Information Disclosure Stmt | 2806 | 1 | 90 | 90 |
| | | **Total in USD ($)** | | **90** |

| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 15860971 |
| **Application Number:** | 13065553 |
| **International Application Number:** | |
| **Confirmation Number:** | 2262 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Correspondence Address:** | Audrey A. Millemann<br>Weintraub Genshlea Chediak<br>11th Floor<br>400 Capitol Mall<br>Sacramento CA 95814<br>US 9165586033<br>amillemann@weintraub.com |
| **Filer:** | Audrey A. Millemann/Alma Martinez |
| **Filer Authorized By:** | Audrey A. Millemann |
| **Attorney Docket Number:** | 8568/17669 |
| **Receipt Date:** | 23-MAY-2013 |
| **Filing Date:** | 24-MAR-2011 |
| **Time Stamp:** | 21:48:16 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| | |
|---|---|
| Submitted with Payment | yes |
| Payment Type | Deposit Account |
| Payment was successfully received in RAM | $90 |

| | |
|---|---|
| RAM confirmation Number | 6869 |
| Deposit Account | 501176 |
| Authorized User | |

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes)/ Message Digest | Multi Part /.zip | Pages (if appl.) |
|---|---|---|---|---|---|
| 1 | Transmittal Letter | 8568_17669_Supplemental_IDS.pdf | 58609<br>e3e77803f8cb0ca01ab1ab14975a35b80167e6ba | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 2 | Information Disclosure Statement (IDS) Form (SB08) | 8568_17669_Form1449.pdf | 78266<br>3585bad2d1a4baa9a313baf8d848e0885b5ab2a3 | no | 1 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| This is not an USPTO supplied IDS fillable form | | | | | |
| 3 | Amendment/Req. Reconsideration-After Non-Final Reject | 8568_17669_Amendment.pdf | 517402<br>58624a9d3b25657a34dc0cccfde04e3d92e44b6e | no | 18 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 4 | Fee Worksheet (SB06) | fee-info.pdf | 29872<br>176cde9ae7f748f1701cc93aa1f2b19c572699c8 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 684149 | | |

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

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

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

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

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

| | | | |
|---|---|---|---|
| Applicants: | Michael S. Harvey, et al. | ) | |
| | | ) | |
| Serial No.: | 13/065,553 | ) | Art Unit: 1628 |
| | | ) | Examiner: Rei Tsang Shiao |
| Filing Date: | March 24, 2011 | ) | |
| | | ) | |
| For: | Methods and Compositions for the Generation of Peracetic Acid on Site at the Point-of-Use | ) | |

May 23, 2013
Sacramento, California 95814

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

**SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT**

Sir:

Pursuant to Rules 1.97 and 1.98, Applicants submit herewith copies of patents, publications, or other information of which Applicants are aware, as listed on the accompanying Form 1449, which Applicants believe may be material to the examination of this application and with respect to which there may be a duty to disclose.

The filing of this supplemental information disclosure statement and accompanying Form 1449 shall not be construed as a representation that a search has been made (37 C.F.R. 1.97(g)), an admission that the information cited is, or is considered to be, material to patentability, or that no other material information exists.

The filing of this supplemental information disclosure statement and accompanying Form 1449 shall not be construed as an admission against interest in any manner. (Notice of January 9, 1992, 1135 O.G. 13-25, at 25.)



CLEAN CHEMISTRY EXHIBIT 1023
IPR2025-01458 – Page 387

Date: May 23, 2013

Respectfully submitted,

By: /Audrey A. Millemann/
Audrey A. Millemann (Reg. No. 44,942)
Attorney for Applicants
Weintraub Tobin Chediak Coleman Grodin
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(916) 558-6033

PTO/SB/08a (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
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Substitute for form 1449/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 1

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1628 |
| Examiner Name | Rei Tsang Shiao |
| Attorney Docket Number | 8568/17669 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number Number-Kind Code[2] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US- 2010/0196505 A1 | 08-05-2010 | Kaiser | |
| | | US- 2012/0165407 A1 | 06-28-2012 | Gupta | |
| | | US- 2012/0172441 A1 | 07-05-2012 | Li | |
| | | US- 7,919,122 | 11-29-2007 | Okano | |
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**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document Country Code[3]-Number[4]-Kind Code[5] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
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| Examiner Signature | | Date Considered | |
|---|---|---|---|

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

*If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.*

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
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# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | ☐ To be Mailed |
|---|---|---|
| 13/065,553 | 03/24/2011 | |

## APPLICATION AS FILED – PART I

| FOR | (Column 1) NUMBER FILED | (Column 2) NUMBER EXTRA | SMALL ENTITY ☒ RATE ($) | SMALL ENTITY ☒ FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY FEE ($) |
|---|---|---|---|---|---|---|---|
| ☐ BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | X $ = | |
| ☐ APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| ☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | | | | | |
| * If the difference in column 1 is less than zero, enter "0" in column 2. | | | TOTAL | | | TOTAL | |

## APPLICATION AS AMENDED – PART II

| AMENDMENT 05/23/2013 | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | SMALL ENTITY RATE ($) | SMALL ENTITY ADDITIONAL FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| Total (37 CFR 1.16(i)) | * 88 | Minus | ** 91 | = 0 | X $40 = | 0 | OR | X $ = | |
| Independent (37 CFR 1.16(h)) | * 10 | Minus | ***11 | = 0 | X $210 = | 0 | OR | X $ = | |
| ☐ Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| ☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | | | OR | | |
| | | | | | TOTAL ADD'L FEE | 0 | OR | TOTAL ADD'L FEE | |

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

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
/POLIN ANG/

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

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United States Patent and Trademark Office
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

# NOTICE OF ALLOWANCE AND FEE(S) DUE

7590 07/15/2013

AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

| EXAMINER |
|---|
| SHIAO, REI TSANG |

| ART UNIT | PAPER NUMBER |
|---|---|
| 1628 | |

DATE MAILED: 07/15/2013

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

TITLE OF INVENTION: Methods and compositions for the generation of peracetic acid on site at the point-of-use

| APPLN. TYPE | ENTITY STATUS | ISSUE FEE DUE | PUBLICATION FEE DUE | PREV. PAID ISSUE FEE | TOTAL FEE(S) DUE | DATE DUE |
|---|---|---|---|---|---|---|
| nonprovisional | SMALL | $890 | $300 | $0 | $1190 | 10/15/2013 |

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

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

**HOW TO REPLY TO THIS NOTICE:**

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

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

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

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

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

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

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

## PART B - FEE(S) TRANSMITTAL

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

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

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

7590 07/15/2013
AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

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

**Certificate of Mailing or Transmission**

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

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

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

TITLE OF INVENTION: Methods and compositions for the generation of peracetic acid on site at the point-of-use

| APPLN. TYPE | ENTITY STATUS | ISSUE FEE DUE | PUBLICATION FEE DUE | PREV. PAID ISSUE FEE | TOTAL FEE(S) DUE | DATE DUE |
|---|---|---|---|---|---|---|
| nonprovisional | SMALL | $890 | $300 | $0 | $1190 | 10/15/2013 |

| EXAMINER | ART UNIT | CLASS-SUBCLASS |
|---|---|---|
| SHIAO, REI TSANG | 1628 | 514-557000 |

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

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

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

2. For printing on the patent front page, list

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

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

1 _____

2 _____

3 _____

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

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

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

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

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

❑ Issue Fee

❑ Publication Fee (No small entity discount permitted)

❑ Advance Order - # of Copies _____

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

❑ A check is enclosed.

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

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

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

❑ Applicant certifying micro entity status. See 37 CFR 1.29

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

❑ Applicant asserting small entity status. See 37 CFR 1.27

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

❑ Applicant changing to regular undiscounted fee status.

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

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

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Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

7590 07/15/2013

AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

| EXAMINER | |
|---|---|
| SHIAO, REI TSANG | |
| ART UNIT | PAPER NUMBER |
| 1628 | |

DATE MAILED: 07/15/2013

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

The Patent Term Adjustment to date is 162 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 162 day(s).

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

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

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

## Privacy Act Statement

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

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

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

| Notice of Allowability | Application No. 13/065,553 | Applicant(s) HARVEY ET AL. | |
|---|---|---|---|
| | Examiner REI-TSANG SHIAO | Art Unit 1628 | AIA (First Inventor to File) Status No |

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

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

1. ☒ This communication is responsive to *amendment filed on 5/23/2013*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *7-8, 10-25, 28-29, 32-33 and 39, now are 1-23*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   **Certified copies:**

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

   * Certified copies not received: _____.

   **Interim copies:**

   a) ☐ All b) ☐ Some c) ☐ None of the: Interim copies of the priority documents have been received.

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

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

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

**Attachment(s)**

1. ☐ Notice of References Cited (PTO-892)
2. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 5/23/13
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☒ Examiner's Amendment/Comment
6. ☒ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/REI-TSANG SHIAO /
Primary Examiner, Art Unit 1628

## DETAILED ACTION

**1**. Amendment of claims 7-8 and cancelation of claim 9 in the amendment filed on 5/23/2013 is acknowledged. Claims 1-8 and 10-91 are pending in the application.

### *EXAMINER'S AMENDMENT*

**2**. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in a telephone interview with Audrey A. Millemann on June 17, 2013. The application has been amended as follows:

In claim 16, line 2, after "peroxide", delete "and the acetyl precursor", and insert ---triacetin--

In claim 17, line 2, after "peroxide", delete "and the acetyl precursor", and insert ---triacetin--

In claim 18, line 3, after "peroxide", delete "and the acetyl precursor", and insert ---triacetin--

In claim 19, line 1, after "wherein", delete "the acetyl precursor is triacetin"

Delete claims 1-6, 26-27, 30-31, 34-38 and 40-91.

### *Reasons for Allowance*

**3.** The rejection of claims 7-8, 10-25, 28-29, 32-33 and 39 under 35 U.S.C. 112, first or second paragraph has been overcome in the amendment filed on 05/23/2013. Since claim 9 has been canceled, the reject ion of claim 9 under 35 U.S.C. 112, first or second paragraph has been obviated herein.

**4.** Claims 7-8, 10-25, 28-29, 32-33 and 39 are neither anticipated nor rendered obvious over the art of record, and therefore are allowable. A suggestion for modification of a reference to obtain the instant processes has not been found. Claims 7-8, 10-25, 28-29, 32-33 and 39 are allowed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled “Comments on Statement of Reasons for Allowance”.

### *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Rei-tsang Shiao whose telephone number is (571) 272-0707. The examiner can normally be reached on 8:30 AM - 5:00 PM. If attempts to reach the examiner by telephone are unsuccessful, the examiner’s supervisor, Brandon Fetterolf, can be reached on (571)272-2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information

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

/REI-TSANG SHIAO/

Rei-tsang Shiao, Ph.D.
Primary Examiner
Art Unit 1628

June 19, 2013

UNITED STATES PATENT AND TRADEMARK OFFICE

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

# BIB DATA SHEET

**CONFIRMATION NO. 2262**

| SERIAL NUMBER | FILING or 371(c) DATE<br>RULE | CLASS | GROUP ART UNIT | ATTORNEY DOCKET NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | 514 | 1628 | 8568/17669 |

**APPLICANTS**
Michael S. Harvey, Modesto, CA;
Jonathan N. Howarth, Modesto, CA;

** **CONTINUING DATA** **********

** **FOREIGN APPLICATIONS** **********

** **IF REQUIRED, FOREIGN FILING LICENSE GRANTED** ** ** SMALL ENTITY **
04/08/2011

| Foreign Priority claimed ☐ Yes ☑ No<br>35 USC 119(a-d) conditions met ☐ Yes ☑ No<br>Verified and Acknowledged /REI-TSANG SHIAO/ Examiner's Signature | ☐ Met after Allowance<br>R.S. Initials | STATE OR COUNTRY | SHEETS DRAWINGS | TOTAL CLAIMS | INDEPENDENT CLAIMS |
|---|---|---|---|---|---|
| | | CA | 1 | 91 | 11 |

**ADDRESS**

Audrey A. Millemann
Weintraub Genshlea Chediak
11th Floor
400 Capitol Mall
Sacramento, CA 95814
UNITED STATES

23

**TITLE**

Methods and compositions for the generation of peracetic acid on site at the point-of-use

| FILING FEE RECEIVED | | |
|---|---|---|
| 3271 | FEES: Authority has been given in Paper<br>No._____ to charge/credit DEPOSIT ACCOUNT<br>No._____ for following: | ☐ All Fees<br>☐ 1.16 Fees (Filing)<br>☐ 1.17 Fees (Processing Ext. of time)<br>☐ 1.18 Fees (Issue)<br>☐ Other _____<br>☐ Credit |

PTO/SB/08a (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
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Substitute for form 1449/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 1

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1628 |
| Examiner Name | Rei Tsang Shiao |
| Attorney Docket Number | 8568/17669 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US- 2010/0196505 A1 | 08-05-2010 | Kaiser | |
| | | US- 2012/0165407 A1 | 06-28-2012 | Gupta | |
| | | US- 2012/0172441 A1 | 07-05-2012 | Li | |
| | | US- 7,919,122 | 11-29-2007 | Okano | |
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**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3]-Number[4]-Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
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| Examiner Signature | /Rei Tsang Shiao/ | Date Considered | 6/17/2013 |
|---|---|---|---|

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

*If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.*

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /R.S./

**EAST Search History**

**EAST Search History (Prior Art)**

| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
|---|---|---|---|---|---|---|
| L1 | 1809 | (514/557).CCLS. | USPAT; USOCR | OR | OFF | 2013/06/19 11:18 |

**EAST Search History (Interference)**

| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
|---|---|---|---|---|---|---|
| L2 | 6 | (514/557).CCLS. | UPAD | OR | OFF | 2013/06/19 11:18 |

**6/19/2013 11:19:12 AM**

## Search Notes

| Application/Control No. | Applicant(s)/Patent under Reexamination | |
|---|---|---|
| 13/065,553 | HARVEY ET AL. | |
| **Examiner** | **Art Unit** | |
| REI-TSANG SHIAO | 1628 | |

| SEARCHED | | | |
|---|---|---|---|
| Class | Subclass | Date | Examiner |
| 514 | 557 | 6/19/2013 | R.S. |
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| INTERFERENCE SEARCHED | | | |
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| Class | Subclass | Date | Examiner |
| **514** | **557** | **6/19/2013** | **R.S.** |
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| SEARCH NOTES (INCLUDING SEARCH STRATEGY) | | |
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| | DATE | EXMR |
| EAST class/subclass | 6/19/2013 | R.S. |
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| Issue Classification | Application/Control No. 13/065,553 | Applicant(s)/Patent under Reexamination HARVEY ET AL. |
|---|---|---|
| | Examiner REI-TSANG SHIAO | Art Unit 1628 |

# ISSUE CLASSIFICATION

| ORIGINAL | | INTERNATIONAL CLASSIFICATION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CLASS | SUBCLASS | CLAIMED | | | | | NON-CLAIMED | | | | | | |
| 514 | 557 | A | 61 | K | 31 | /19 | | | | / | | | |
| CROSS REFERENCES | | | | | | / | | | | / | | | |
| CLASS | SUBCLASS (ONE SUBCLASS PER BLOCK) | | | | | / | | | | / | | | |
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| (Assistant Examiner) (Date) | /Rei-tsang Shiao/ 6/19/2013 | Total Claims Allowed: 23 | |
|---|---|---|---|
| (Legal Instruments Examiner) (Date) | (Primary Examiner) (Date) | O.G. Print Claim(s) 1 | O.G. Print Fig. NONE |

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

| Final | Original | Final | Original | Final | Original | Final | Original | Final | Original | Final | Original | Final | Original |
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| | 3 | 22 | 33 | | 63 | | 93 | | 123 | | 153 | | 183 |
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| | 5 | | 35 | | 65 | | 95 | | 125 | | 155 | | 185 |
| | 6 | | 36 | | 66 | | 96 | | 126 | | 156 | | 186 |
| 1 | 7 | | 37 | | 67 | | 97 | | 127 | | 157 | | 187 |
| 2 | 8 | | 38 | | 68 | | 98 | | 128 | | 158 | | 188 |
| | 9 | 23 | 39 | | 69 | | 99 | | 129 | | 159 | | 189 |
| 3 | 10 | | 40 | | 70 | | 100 | | 130 | | 160 | | 190 |
| 4 | 11 | | 41 | | 71 | | 101 | | 131 | | 161 | | 191 |
| 5 | 12 | | 42 | | 72 | | 102 | | 132 | | 162 | | 192 |
| 6 | 13 | | 43 | | 73 | | 103 | | 133 | | 163 | | 193 |
| 7 | 14 | | 44 | | 74 | | 104 | | 134 | | 164 | | 194 |
| 8 | 15 | | 45 | | 75 | | 105 | | 135 | | 165 | | 195 |
| 9 | 16 | | 46 | | 76 | | 106 | | 136 | | 166 | | 196 |
| 10 | 17 | | 47 | | 77 | | 107 | | 137 | | 167 | | 197 |
| 11 | 18 | | 48 | | 78 | | 108 | | 138 | | 168 | | 198 |
| 12 | 19 | | 49 | | 79 | | 109 | | 139 | | 169 | | 199 |
| 13 | 20 | | 50 | | 80 | | 110 | | 140 | | 170 | | 200 |
| 14 | 21 | | 51 | | 81 | | 111 | | 141 | | 171 | | 201 |
| 15 | 22 | | 52 | | 82 | | 112 | | 142 | | 172 | | 202 |
| 16 | 23 | | 53 | | 83 | | 113 | | 143 | | 173 | | 203 |
| 17 | 24 | | 54 | | 84 | | 114 | | 144 | | 174 | | 204 |
| 18 | 25 | | 55 | | 85 | | 115 | | 145 | | 175 | | 205 |
| | 26 | | 56 | | 86 | | 116 | | 146 | | 176 | | 206 |
| | 27 | | 57 | | 87 | | 117 | | 147 | | 177 | | 207 |
| 19 | 28 | | 58 | | 88 | | 118 | | 148 | | 178 | | 208 |
| 20 | 29 | | 59 | | 89 | | 119 | | 149 | | 179 | | 209 |
| | 30 | | 60 | | 90 | | 120 | | 150 | | 180 | | 210 |

## PART B - FEE(S) TRANSMITTAL

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

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

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

7590 07/15/2013
AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

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

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

| | |
|---|---|
| Audrey A. Millemann | (Depositor's name) |
| /Audrey A. Millemann/ | (Signature) |
| August 14, 2013 | (Date) |

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 | 2262 |

TITLE OF INVENTION: Methods and compositions for the generation of peracetic acid on site at the point-of-use

| APPLN. TYPE | ENTITY STATUS | ISSUE FEE DUE | PUBLICATION FEE DUE | PREV. PAID ISSUE FEE | TOTAL FEE(S) DUE | DATE DUE |
|---|---|---|---|---|---|---|
| nonprovisional | SMALL | $890 | $300 | $0 | $1190 | 10/15/2013 |

| EXAMINER | ART UNIT | CLASS-SUBCLASS |
|---|---|---|
| SHIAO, REI TSANG | 1628 | 514-557000 |

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

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

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

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

(A) NAME OF ASSIGNEE: Enviro Tech Chemical Services, Inc.
(B) RESIDENCE: (CITY and STATE OR COUNTRY): Modesto, California

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

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

4b. Payment of Fee(s): (Please first reapply any previously paid issue fee shown above)
☐ A check is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number 501176 (enclose an extra copy of this form).

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

☐ Applicant certifying micro entity status. See 37 CFR 1.29

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

☐ Applicant asserting small entity status. See 37 CFR 1.27

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

☐ Applicant changing to regular undiscounted fee status.

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

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature /Audrey A. Millemann/ Date August 14, 2013

Typed or printed name Audrey A. Millemann Registration No. 44,942

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

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# Electronic Patent Application Fee Transmittal

| | |
|---|---|
| **Application Number:** | 13065553 |
| **Filing Date:** | 24-Mar-2011 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Filer:** | Audrey A. Millemann/Alma Martinez |
| **Attorney Docket Number:** | 8568/17669 |

Filed as Small Entity

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

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Basic Filing:** | | | | |
| **Pages:** | | | | |
| **Claims:** | | | | |
| **Miscellaneous-Filing:** | | | | |
| **Petition:** | | | | |
| **Patent-Appeals-and-Interference:** | | | | |
| **Post-Allowance-and-Post-Issuance:** | | | | |
| Utility Appl Issue Fee | 2501 | 1 | 890 | 890 |
| Publ. Fee- Early, Voluntary, or Normal | 1504 | 1 | 300 | 300 |

| Description | Fee Code | Quantity | Amount | Sub-Total in USD($) |
|---|---|---|---|---|
| **Extension-of-Time:** | | | | |
| **Miscellaneous:** | | | | |
| | | | **Total in USD ($)** | **1190** |

| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 16594464 |
| **Application Number:** | 13065553 |
| **International Application Number:** | |
| **Confirmation Number:** | 2262 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Correspondence Address:** | AUDREY A. MILLEMANN<br>WEINTRAUB GENSHLEA CHEDIAK<br>11TH FLOOR<br>400 CAPITOL MALL<br>SACRAMENTO CA 95814<br>US 9165586033<br>amillemann@weintraub.com |
| **Filer:** | Audrey A. Millemann/Alma Martinez |
| **Filer Authorized By:** | Audrey A. Millemann |
| **Attorney Docket Number:** | 8568/17669 |
| **Receipt Date:** | 14-AUG-2013 |
| **Filing Date:** | 24-MAR-2011 |
| **Time Stamp:** | 20:39:45 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| | |
|---|---|
| Submitted with Payment | yes |
| Payment Type | Deposit Account |
| Payment was successfully received in RAM | $1190 |

| | |
|---|---|
| RAM confirmation Number | 7865 |
| Deposit Account | 501176 |
| Authorized User | |

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Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes)/ Message Digest | Multi Part /.zip | Pages (if appl.) |
|---|---|---|---|---|---|
| 1 | Issue Fee Payment (PTO-85B) | 8568_17669_Fee_Transmittal.pdf | 127470<br>271370c8522f3985b1b1b8e0562ccaafff8eb87f | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| 2 | Fee Worksheet (SB06) | fee-info.pdf | 31552<br>577c00173dfa3072c771a65d6027779fbdeef491 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 159022 | | |

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

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

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

# PRINTER RUSH

## (PTO ASSISTANCE)

| | | | | | |
|---|---|---|---|---|---|
| **Application:** | 13065553 | **Examiner:** | Shiao | **GAU:** | 1628 |
| **From:** | Lisa Kraft-Hegarty | **Location:** | IDC | **Creation Date:** | 08/16/2013 |

Tracking #: Week Date: 07/15/2013

| DOC CODE | DOC DATE | MISCELLANEOUS |
|---|---|---|
| ☐ 1449 | | ☐ Continuing Data |
| ☐ IDS | | ☐ Foreign Priority |
| ☒ CLM | 05/23/2013 | ☐ Document Legibility |
| ☐ IIFW/FWCLM | | ☐ Fees |
| ☐ SRFW | | ☐ Petition (TC) |
| ☐ DRW | | ☐ Other |
| ☐ OATH | | |
| ☐ 312 | | |
| ☐ SPEC | | |

**[RUSH] Message:**

Renumbered claims 3 and 6 (original claims 10 and 13) both depend on original claim 9 which has been canceled per CLM 05/23/2013.
Thank you.

**[XRUSH] Response:**

Initials: _____

Examiner: PUBS contacts - for DESIGNS: Don Fairchild, 703-756-1566; for ALL OTHER files: Bernadette Queen, 703-756-1565.
NOTE: This form will be included as part of the official USPTO record with the response document coded as XRUSH.
REV: Oct 11

# PRINTER RUSH

## (PTO ASSISTANCE)

| | | | | | |
|---|---|---|---|---|---|
| **Application:** | 13065553 | **Examiner:** | Shiao | **GAU:** | 1628 |
| **From:** | Lisa Kraft-Hegarty | **Location:** | IDC | **Creation Date:** | 08/16/2013 |

Tracking #: Week Date: 07/15/2013

| DOC CODE | DOC DATE | MISCELLANEOUS |
|---|---|---|
| ☐ 1449 | | ☐ Continuing Data |
| ☐ IDS | | ☐ Foreign Priority |
| ☒ CLM | 05/23/2013 | ☐ Document Legibility |
| ☐ IIFW/FWCLM | | ☐ Fees |
| ☐ SRFW | | ☐ Petition (TC) |
| ☐ DRW | | ☐ Other |
| ☐ OATH | | |
| ☐ 312 | | |
| ☐ SPEC | | |

**[RUSH] Message:**

Renumbered claims 3 and 6 (original claims 10 and 13) both depend on original claim 9 which has been canceled per CLM 05/23/2013.
Thank you.

**[XRUSH] Response:**

Renumbered claim 3 and 6 (original claim 10 and 13) should depend on claim 7.

R.S.

Initials: _____

Examiner: PUBS contacts - for DESIGNS: Don Fairchild, 703-756-1566; for ALL OTHER files: Bernadette Queen, 703-756-1565.
NOTE: This form will be included as part of the official USPTO record with the response document coded as XRUSH.
REV: Oct 11

PTO/SB/08a (07-09)
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Substitute for form 1449/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 1

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1628 |
| Examiner Name | Rei Tsang Shiao |
| Attorney Docket Number | 8568/17669 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number Number-Kind Code[2] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US- 2010/0196505 A1 | 08-05-2010 | Kaiser | |
| | | US- 2012/0165407 A1 | 06-28-2012 | Gupta | |
| | | US- 2012/0172441 A1 | 07-05-2012 | Li | |
| | | US- 7,919,122 | ~~11-29-2007~~ | Okano et al. 04-2011 | |
| | | US- | | | |
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Change(s) applied to document, /R.M.L./ 8/22/2013

**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document Country Code[3]-Number[4]-Kind Code[5] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
|---|---|---|---|---|---|---|
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| Examiner Signature | /Rei Tsang Shiao/ | Date Considered | 6/17/2013 |
|---|---|---|---|

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

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ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /R.S./

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 2

| Complete if Known | |
|---|---|
| Application Number | 13/065,553 |
| Filing Date | March 24, 2011 |
| First Named Inventor | Michael S. Harvey |
| Art Unit | 1761 |
| Examiner Name | |
| Attorney Docket Number | 8568/17769 |

**U. S. PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US- 3,956,159 | 05-11-1976 | Jones | |
| | | US- 5,122,538 | 06-16-1992 | Lokkesmoe, et al. | |
| | | US- 5,977,403 | 11-02-1999 | Byers | |
| | | US- 6,171,551 B1 | 01-09-2001 | Malchesky, et al. | |
| | | US- 6,262,013 B1 | 07-17-2001 | Smith, et al. | |
| | | US- 6,387,236 B2 | 05-14-2002 | Nordman, et al. | |
| | | US- 7,012,154 B2 03 | ~~02-02~~-2006 | Vineyard, et al. | |
| Change(s) applied | | US- 7,723,083 B2 | ~~01-01-2009~~ | DiCosimo, et al. 05-2010 | |
| to document, | | US- 7,271,137 B2 | ~~05-26-2005~~ | Tucker, et al. 09-2007 | |
| /R.M.L./ | | US- 2004/0245116 A1 | 12-09-2004 | Ohsaka, et al. | |
| 8/22/2013 | | US- 2005/0118940 A1 | 06-02-2005 | Hilgren, et al. | |
| | | US- ~~2007/0082832~~ A1 | 04-12-2007 | DiCosimo, et al. | 2009/0043123 |
| | | US- 2009/0175956 A1 | 07-09-2009 | Buschmann, et al. | |
| | | US- 2009/0043132 A1 | 02-12-2009 | Copenhafer, et al. | |
| | | US- 2009/0314652 A1 | 12-24-2009 | Buschmann, et al. | |
| | | US- 2010/0196505 A1 | 08-05-2010 | Kaiser, et al. | |
| | | US- 2010/0227000 A1 | 09-09-2010 | Ames, et al. | |
| | | US- 3,432,546 | ~~11-03-1964~~ | Oringer, et al. 03-1969 | |
| | | US- | | | |

**FOREIGN PATENT DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3]-Number[4]-Kind Code[5] (if known) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear | T[6] |
|---|---|---|---|---|---|---|
| | 1 | EP 0 563 460 B1 | 07-01-1998 | The Procter & Gamble Co. | | |
| | 2 | WO 01/46519 A1 | 06-28-2001 | Warwick International | | |
| | 3 | WO 2008/140988 A1 | 11-20-2008 | Danisco US Inc. | | |
| | 4 | WO 2010/005607 A2 | 01-14-2010 | Electron Research & Dev. | | |
| | | | | | | |
| | | | | | | |

| Examiner Signature | | Date Considered | |
|---|---|---|---|

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

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United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | ISSUE DATE | PATENT NO. | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 13/065,553 | 10/01/2013 | 8546449 | 8568/17669 | 2262 |

7590 09/11/2013

AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

# ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

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

The Patent Term Adjustment is 162 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

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

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

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

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

Michael S. Harvey, Modesto, CA;
Jonathan N. Howarth, Modesto, CA;

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Doc Code: PA..
Document Description: Power of Attorney

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# TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

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

| | |
|---|---|
| Application Number | 13/065553 |
| Filing Date | 03/24/2011 |
| First Named Inventor | Michael S. Harvey |
| Title | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| Art Unit | 1628 |
| Examiner Name | Not Assigned |
| Attorney Docket Number | LZA-273 (LP3623US00) |

**SIGNATURE of Applicant or Patent Practitioner**

| | | | |
|---|---|---|---|
| Signature | /timothy a. cassidy/ | Date (Optional) | |
| Name | Timothy A. Cassidy | Registration Number | 38024 |
| Title (if Applicant is a juristic entity) | | | |
| Applicant Name (if Applicant is a juristic entity) | | | |

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

☑ *Total of 1 forms are submitted.

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Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
Approved for use through 03/31/2021. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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# POWER OF ATTORNEY BY APPLICANT

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

| Application Number | Filing Date |
|---|---|
| | |

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 22827

**OR**

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

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

☐ The address associated with the above-mentioned Customer Number

**OR**

☐ The address associated with Customer Number: 22827

**OR**

| | | | | | |
|---|---|---|---|---|---|
| ☐ Firm or Individual Name | Dority & Manning, P.A. | | | | |
| Address | PO Box 1449 | | | | |
| City | Greenville | State | SC | Zip | 29602 |
| Country | US | | | | |
| Telephone | 864-271-1592 | Email | docketing@dority-manning.com | | |

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

ENVIRO TECH CHEMICAL SERVICES, INC.

☐ Inventor or Joint Inventor (title not required below)

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

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

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

**SIGNATURE of Applicant for Patent**

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

| | | | |
|---|---|---|---|
| Signature | /Julie Gallucci/ | Date (Optional) | 1/19/23 |
| Name | Julie Gallucci | | |
| Title | President Enviro Tech | | |

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

☑ Total of 1 forms are submitted.

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| Electronic Acknowledgement Receipt | |
|---|---|
| **EFS ID:** | 47416316 |
| **Application Number:** | 13065553 |
| **International Application Number:** | |
| **Confirmation Number:** | 2262 |
| **Title of Invention:** | Methods and compositions for the generation of peracetic acid on site at the point-of-use |
| **First Named Inventor/Applicant Name:** | Michael S. Harvey |
| **Correspondence Address:** | AUDREY A. MILLEMANN<br>WEINTRAUB GENSHLEA CHEDIAK<br>11TH FLOOR<br>400 CAPITOL MALL<br>SACRAMENTO CA 95814<br>US 9165586033<br>amillemann@weintraub.com |
| **Filer:** | Timothy A. Cassidy/Taylor Holden |
| **Filer Authorized By:** | Timothy A. Cassidy |
| **Attorney Docket Number:** | 8568/17669 |
| **Receipt Date:** | 24-JAN-2023 |
| **Filing Date:** | 24-MAR-2011 |
| **Time Stamp:** | 10:32:24 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

| | |
|---|---|
| Submitted with Payment | no |

## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes)/ Message Digest | Multi Part /.zip | Pages (if appl.) |
|---|---|---|---|---|---|
| 1 | Power of Attorney | LZA-273_POA.PDF | 381883<br>67b177a85e46b26df1c7bf47a8834164b7c41e96 | no | 2 |
| **Warnings:** | | | | | |
| **Information:** | | | | | |
| | | **Total Files Size (in bytes):** | 381883 | | |

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

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

**New International Application Filed with the USPTO as a Receiving Office**

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UNITED STATES PATENT AND TRADEMARK OFFICE

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www.uspto.gov

| APPLICATION NUMBER | FILING OR 371(C) DATE | FIRST NAMED APPLICANT | ATTY. DOCKET NO./TITLE |
|---|---|---|---|
| 13/065,553 | 03/24/2011 | Michael S. Harvey | 8568/17669 |

**CONFIRMATION NO. 2262**

**IMPROPER CPOA LETTER**

AUDREY A. MILLEMANN
WEINTRAUB GENSHLEA CHEDIAK
11TH FLOOR
400 CAPITOL MALL
SACRAMENTO, CA 95814

*OC000000137315040*

Date Mailed: 02/06/2023

## NOTICE REGARDING POWER OF ATTORNEY

This is in response to the power of attorney filed 01/24/2023. The power of attorney in this application is not accepted for the reason(s) listed below:

- The power of attorney is from an assignee and the statement required by 37 CFR 3.73(c) has not been received.

/zabraha/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

22827
DORITY & MANNING, P.A.
POST OFFICE BOX 1449
GREENVILLE, SC 29602-1449
UNITED STATES

Doc Code: MFEE.C.AD
Document Description: Maintenance Fee Address Change

PTO/AIA/47 (11-21)
Approved for use through 11/30/2024. OMB 0651-0016
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# "FEE ADDRESS" INDICATION FORM

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**INSTRUCTIONS:** The issue fee must have been paid for the application(s) listed on this form. In addition, only an address represented by a Customer Number can be established as the fee address for maintenance fee purposes (hereafter, fee address). A fee address should be established when correspondence related to maintenance fees should be mailed to a different address than the correspondence address for the application.

**When to check the first box below:** If you have a Customer Number to represent the fee address.

**When to check the second box below:** If you have no Customer Number representing the desired fee address, in which case a completed Request for Customer Number (PTO/SB/125) must be attached to this form. For more information on Customer Numbers, see the Manual of Patent Examining Procedure (MPEP) § 403.

For the following listed application(s), please recognize as the "Fee Address" under the provisions of 37 CFR 1.363 the address associated with:

☑ Customer Number: 22827

***OR***

☐ The attached Request for Customer Number form (PTO/SB/125)

| PATENT NUMBER (if known) | APPLICATION NUMBER |
|---|---|
| 8,546,449 | 13/065,553 |

Completed by (check one):

☐ Applicant/Inventor

☑ Attorney or Agent of record 38,024 (Reg. No.)

☐ Assignee of record of the entire interest. See 37 CFR 3.71. Statement under 37 CFR 3.73(c) (Form PTO/AIA/96) is enclosed or was filed on _____ (Date)

/Tim Cassidy/
Signature

Timothy A. Cassidy
Typed or printed name

864-271-1592
Requester's telephone number

06/08/2023
Date

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. If the assignee is a juristic entity, this form must be signed by a patent practitioner (attorney or agent) of record. Submit multiple forms if more than one signature is required, see below*.

☑ *Total of 1 forms are submitted

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

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | | |
|---|---|---|---|
| Application of: | Michael S. Harvey | Examiner: | N/A |
| Serial Number: | 13/065,553 | Group Art Unit: | 1628 |
| Filed: | 04/16/2007 | Customer Number: | 22827 |
| Confirmation No.: | 2262 | Deposit Account: | 04-1403 |
| Title: | Methods and compositions for the generation of peracetic acid on site at the point-of-use | Docket Number: | LZA-273 |

## NOTIFICATION OF LOSS OF ENTITLEMENT TO SMALL ENTITY STATUS

U.S. Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Please be notified that the Applicant, ENVIRO TECH CHEMICAL SERVICES, INC., has lost its entitlement to small entity status for the above-captioned application.

The Office is invited and encouraged to telephone the undersigned if any issues remain after consideration of this notification.

Respectfully submitted,

DORITY & MANNING, P.A.

June 8, 2023
Date

/Tim Cassidy/
Timothy A. Cassidy
Registration Number: 38,024

Post Office Box 1449
Greenville, SC 29602
Telephone: (864) 271-1592
Facsimile: (864) 233-7342 - Fax

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313 on:

DATE: June 8, 2023

NAME: R. Taylor Holden

SIGNATURE: /r. taylor holden/

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
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# ELECTRONIC ACKNOWLEDGEMENT RECEIPT

| APPLICATION # | RECEIPT DATE / TIME | ATTORNEY DOCKET # |
|---|---|---|
| **13/065,553** | **06/08/2023 02:58:51 PM ET** | **8568/17669** |

## Title of Invention

Methods and compositions for the generation of peracetic acid on site at the point-of-use

## Application Information

| | | | |
|---|---|---|---|
| APPLICATION TYPE | Utility - Nonprovisional Application under 35 USC 111(a) | PATENT # | 8546449 |
| CONFIRMATION # | 2262 | FILED BY | Taylor Holden |
| PATENT CENTER # | 62233109 | FILING DATE | 03/24/2011 |
| CUSTOMER # | – | FIRST NAMED INVENTOR | Michael S. Harvey |
| CORRESPONDENCE ADDRESS | AUDREY A. MILLEMANN,<br>WEINTRAUB GENSHLEA CHEDIAK<br>11TH FLOOR, 400 CAPITOL MALL<br>SACRAMENTO, CALIFORNIA 95814<br>UNITED STATES | AUTHORIZED BY | Tim Cassidy |

## Documents

**TOTAL DOCUMENTS: 2**

| DOCUMENT | | PAGES | DESCRIPTION | SIZE (KB) |
|---|---|---|---|---|
| LZA-273_Change-of-EntityStatus_FeeAddress.PDF | | 2 | - | 361 KB |
| LZA-273_Change-of-EntityStatus_FeeAddress-SES.LOSS.pdf | (1-1) | 1 | Notification of loss of entitlement to small entity status | 80 KB |
| LZA-273_Change-of-EntityStatus_FeeAddress-C.AD.pdf | (2-2) | 1 | Change of Address | 247 KB |

## Digest

| DOCUMENT | MESSAGE DIGEST(SHA-512) |
|---|---|
| LZA-273_Change-of-EntityStatus_FeeAddress.PDF | 9C8D83063BC367D908D26FEC909C08FAE9B79E6E30B1F132D2C1FE7CE42150DF59D80B136F2B83C6FF9B50FE98A82A39EA29EECD11E6996F9E014F3D78BF1733 |
| LZA-273_Change-of-EntityStatus_FeeAddress-SES.LOSS.pdf | 0DC583BDB6771A3D86462124E422FE26C9D530AC8D652A7342ADD9469A8E02C59CC5B16C011D7771D433BECFE03C238E09BEFECF8B9ACF56940F03995C552456 |
| LZA-273_Change-of-EntityStatus_FeeAddress-C.AD.pdf | B744C423B7492A4CFA8CCCA56F1E3C76A2AA3DD7BF52B81091DAA41351817A8CBA2DB1C331811A41ADFBE05D10A0042306E24749533725C894504726FC6AECF8 |

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