

EXHIBIT 2003

Complaint and Exhibits

UNITED STATES DISTRICT COURT
WESTERN DISTRICT OF TEXAS
AUSTIN DIVISION

ENVIROTECH CHEMICAL
SERVICES, INC.

Plaintiff,

v.

CLEAN CHEMISTRY, INC.,

Defendant.

Case No. 1:24-cv-1313

Jury Trial Demanded

COMPLAINT

Plaintiff EnviroTech Chemical Services, Inc., by and through its undersigned counsel, brings this action for patent infringement against Clean Chemistry, Inc., and alleges as follows:

PARTIES

1. EnviroTech Chemical Services, Inc. (“EnviroTech”), is a corporation organized and existing under the laws of the State of California, having a principal place of business at 500 Winmoore Way, Modesto, California 95358.

2. Defendant Clean Chemistry, Inc. (“Clean Chemistry” or “Defendant”) is a corporation organized and existing under the laws of the State of Delaware, with a principal place of business at 6107 S. Country Road 1273, Midland, Texas 79706.

FACTUAL ALLEGATIONS

Background of EnviroTech

3. EnviroTech develops and manufactures chemical solutions, focusing on safe and effective antimicrobial formulations. For more than 30 years, EnviroTech has serviced several industries, including industrial water treatment, meat and poultry processing, agriculture, oil and gas, and wastewater treatment.

4. EnviroTech has a storied reputation as an industry-leading innovator of peracetic acid, which is an environmentally friendly and versatile disinfectant.

5. In connection with its research and development and efforts to improve its peracetic acid solutions, EnviroTech has developed innovative processes, reagents, and intermediate solutions, including those protected by the valid and subsisting United States patents referenced below.

Jurisdiction and Venue

6. This is an action for patent infringement arising under the patent laws of the United States, 35 U.S.C. § 1, et seq., including 35 U.S.C. § 271. This Court has original and exclusive subject matter jurisdiction over the patent infringement claims for relief under 28 U.S.C. §§ 1331, 1338(a).

7. Personal jurisdiction exists generally over Clean Chemistry because Clean Chemistry is a corporation organized and existing under the laws of the State

of Delaware, with a principal place of business in the Western District of Texas (“District”).

8. Venue is proper in this Court under 28 U.S.C. § 1391 as well as 28 U.S.C. § 1400(b) because Clean Chemistry resides in the District, where Clean Chemistry is a corporation organized under the laws of the State of Delaware with a principal place of business in the District. Clean Chemistry committed at least one act of infringement in this District, and has a physical location in the District from which it conducts business. Furthermore, a substantial part of the events or omissions giving rise to the claims pleaded herein occurred within the District, or a substantial part of property that is the subject of this action is situated within the District.

The Patents-in-Suit

9. EnviroTech is the owner of the entire right, title, and interest in and to U.S. Patent No. 8,546,449 (the “‘449 Patent”), entitled “Methods and Compositions for the Generation of Peracetic Acid On Site at the Point-Of-Use,” which was duly issued by the United States Patent and Trademark Office on October 1, 2013. A copy of the ‘449 Patent is attached as Exhibit A.

10. EnviroTech is the owner of the entire right, title, and interest in and to U.S. Patent No. 9,363,997 (the “‘997 Patent”), entitled “Methods and Compositions for the Generation of Peracetic Acid On Site at the Point-Of-Use,”

which was duly issued by the United States Patent and Trademark Office on June 14, 2016. A copy of the ‘997 Patent is attached as Exhibit B.

11. EnviroTech is the owner of the entire right, title, and interest in and to U.S. Patent No. 9,730,443 (the “‘443 Patent”), entitled “Methods and Compositions for the Generation of Peracetic Acid On Site at the Point-Of-Use,” which was duly issued by the United States Patent and Trademark Office on August 15, 2017. A copy of the ‘443 Patent is attached as Exhibit C.

12. EnviroTech is the owner of the entire right, title, and interest in and to U.S. Patent No. 9,737,072 (the “‘072 Patent”), entitled “Methods and Compositions for the Generation of Peracetic Acid On Site at the Point-Of-Use,” which was duly issued by the United States Patent and Trademark Office on August 22, 2021. A copy of the ‘072 Patent is attached as Exhibit D.

13. On May 20, 2024, EnviroTech sent a letter to Clean Chemistry informing Clean Chemistry of the ‘449 Patent, the ‘997 Patent, the ‘443 Patent, and the ‘072 Patent, also requesting that Clean Chemistry cease and desist all infringing activities. A copy of the May 20, 2024 letter is attached as Exhibit E.

Defendant’s Wrongful Conduct

14. Clean Chemistry manufactures, uses, imports, offers for sale, and/or sells peracetic acid products under the Clean Chemistry trade name throughout the

United States. Said products directly compete against the offerings from EnviroTech.

15. Defendant, under the Clean Chemistry name, has been and is currently making, using, offering for sale, importing, selling, and/or distributing products that infringe at least one claim of the ‘449 Patent, the ‘997 Patent, the ‘443 Patent, and the ‘072 Patent.

16. Defendant offers for sale certain peracetic acid products that infringe EnviroTech’s rights including by way of example, but not limited to, PeroxyMAX (“Accused Product”). (See, Exhibit F - <https://cleanchemi.com/peroxymax>) (hereinafter “Product Webpage”).

17. On information and belief, Defendant manufactures the Accused Product according to the process set forth in Defendant’s Environmental Assessment for Food Contact Notification FCN 2352 submitted to the United States Food and Drug Administration on February 1, 2024 (“Accused Process”). (See, Exhibit G - <https://www.fda.gov/media/177359/download>) (hereinafter “FCN”).

18. As detailed below, Defendant has directly infringed one or more claims of the ‘449 Patent, the ‘997 Patent, the ‘443 Patent, and the ‘072 Patent by intentionally developing, making, using, marketing, advertising, providing,

sending, importing, distributing, and/or selling the Accused Product, which is manufactured according to the Accused Process.

A. The ‘449 Patent

19. The Accused Process includes all elements of, for example, claim 1 of the ‘449 Patent.

20. By way of example, claim 1 of the ‘449 Patent recites “[a] method of generating non-equilibrium solution of peracetic acid.”

21. The FCN states that “the [food contact substance] is prepared in a non-equilibrium process that produces [peracetic acid].” (Exhibit G, page 9).

On-demand generation of the FCS eliminates the need to incorporate a stabilizer such as 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) in the formulation. As described below, the FCS is prepared in a non-equilibrium process that produces PAA that is immediately applied in the desired concentration. No stabilizers are contained in this FCS since it is produced and used on-demand.

Figure 1

22. The food contact substance referred to in the FCN is the Accused Product, which is a peracetic acid (PAA) solution. Thus, in stating that “the FCS is prepared in a non-equilibrium process that produces PAA,” the FCN specifies that the method disclosed therein is utilized to form a non-equilibrium peracetic acid.

23. The food contact substance referred to in the FCN is the Accused Product, which is a peracetic acid (PAA) solution. Thus, in stating that “the FCS is prepared in a non-equilibrium process that produces PAA,” the FCN specifies that the method disclosed therein is utilized to form a non-equilibrium peracetic acid.

24. Claim 1 of the ‘449 Patent further recites the step of “providing water.”

25. The first step in the Accused Process is to provide water to be the base of the Accused Product solution. For example, the FSN states that “[w]ater is fed into [a] generator/mixer” as the first process step. (Exhibit G, page 9).

a. Process Step 1: Preparation of the alkaline substrate

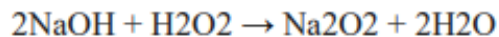
Water is fed into the generator/mixer followed by concentrated sodium hydroxide providing the alkaline environment needed for the next steps.

Figure 2

26. Claim 1 of the ‘449 Patent further recites the step of “introducing a hydrogen peroxide-triacetin solution to the water.”

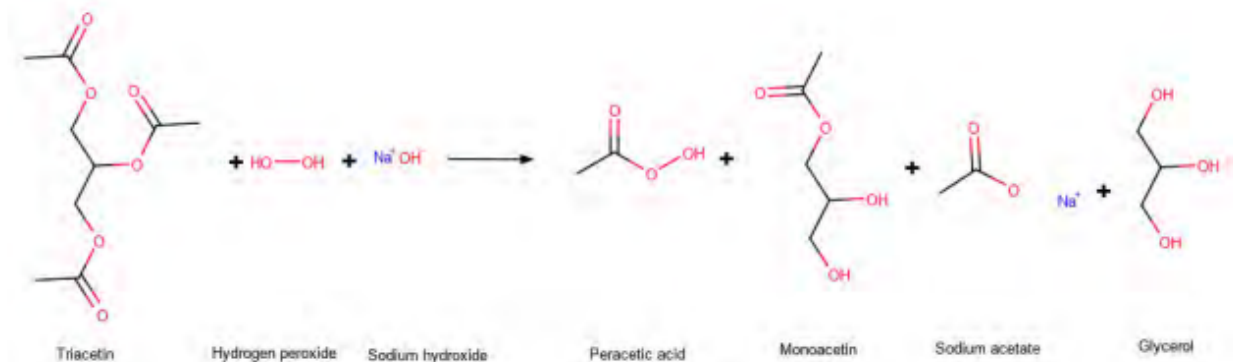
27. The Accused Process also requires addition of hydrogen peroxide and triacetin. For example, the FSN states that, in Step 2 “hydrogen peroxide is blended into the mixture’s alkaline solution” and, in Step 3 “under continuous agitation, triacetin is added to the process.” (Exhibit G, pages 9-10).

b. Process Step 2: Addition of hydrogen peroxide



Next, hydrogen peroxide is blended into the mixer’s alkaline solution and forms an alkaline peroxide solution.

Figure 3

c. Process Step 3: Addition of triacetin

In the next step, under continuous agitation, triacetin is added to the process. Triacetin rapidly reacts with the alkaline peroxide to form an aqueous mixture of PAA. Alkaline pH (pH>10) is used to accelerate the reaction since the hydrogen peroxide anion is a much better nucleophile than hydrogen peroxide. Both the hydrogen peroxide anion, O₂²⁻ and HO⁻ compete in the reaction with triacetin's acetyl groups, the former producing a PAA and the latter producing acetate. The reaction takes place at ambient temperature and pressure.

Figure 4

28. The Accused Process which separately adds hydrogen peroxide and triacetin is equivalent to “introducing a hydrogen peroxide-triacetin solution.” Whether the hydrogen peroxide and triacetin are introduced separately or as a pre-made solution is insubstantia. Thus, separately adding hydrogen peroxide and triacetin is equivalent to “introducing a hydrogen peroxide-triacetin solution” because it performs substantially the same function in substantially the same way to produce substantially the same result.

29. Claim 1 of the ‘997 Patent further recites the step of “mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture.”

30. Claim 1 of the ‘449 Patent further recites the step of “mixing the hydrogen peroxide-triacetin solution and the water to form a mixture.”

31. The FCN detailing the accused process states that “hydrogen peroxide is blended into the mixture’s alkaline solution” and “under continuous agitation, triacetin is added to the process.” (Exhibit G, pages 9-10; Figures 3-4). The “blending” of hydrogen peroxide and addition of triacetin “under continuous agitation” necessarily forms a mixture of the ingredients.

32. Claim 1 of the ‘449 Patent further recites the step of “adding an aqueous source of an alkali metal or early alkali metal hydroxide to the mixture.”

33. The FCN also describes that the Accused Process includes the step of adding “concentrated sodium hydroxide providing an alkaline environment” to the water. (Exhibit G, page 9; Figure 1). Sodium hydroxide is most commonly used in chemical manufacturing as an aqueous solution and is an alkali metal hydroxide.

34. Claim 1 of the ‘449 Patent further recites the step of “forming a reaction medium comprising a non-equilibrium solution of peracetic acid.”

35. When the sodium hydroxide, hydrogen peroxide, and triacetin are all present in the water-based solution, the “[t]riacetin rapidly reacts with the alkaline peroxide to form an aqueous mixture of PAA,” where PAA is defined to mean peracetic acid. (Exhibit G, page 10).

The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with triacetin, the acetyl precursor, to form peracetic acid.

Figure 5

36. The Accused Process which first adds sodium hydroxide to water and subsequently adds hydrogen peroxide and triacetin is equivalent to “adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.” The order in which the sodium hydroxide and the hydrogen peroxide and triacetin is insubstantial. First adding sodium hydroxide to water and then subsequently adding hydrogen peroxide and triacetin is equivalent to “adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture” because it performs substantially the same function in substantially the same way to produce substantially the same result. Switching the order that sodium hydroxide is combined with hydrogen peroxide, triacetin, and water for reaction to form a non-equilibrium solution of peracetic acid will result in the sodium hydroxide performing substantially the same function in substantially the same way to produce substantially the same result.

B. The ‘997 Patent

37. The Accused Process includes all the steps of, for example, claim 1 of the ‘997 Patent.

38. By way of example, claim 1 of the ‘997 Patent recites “[a] method of generating non-equilibrium solution of peracetic acid.”

39. The FCN states that “the [food contact substance] is prepared in a non-equilibrium process that produces PAA,” which is defined to mean peracetic

acid (Exhibit G, page 9; Figure 1). The food contact substance referred to in the FCN is the Accused Product, which is a peracetic acid (PAA) solution. Thus, in stating that “the FCS is prepared in a non-equilibrium process that produces PAA,” the FCN specifies that the method disclosed therein is utilized to form a non-equilibrium peracetic acid.

40. Claim 1 of the ‘997 Patent further recites the step of “providing water.”

41. The first step in the Accused Process is to provide water to be the base of the Accused Product solution. For example, the FSN states that “[w]ater is fed into [a] generator/mixer” as the first process step. (Exhibit G, page 9; Figure 2).

42. Claim 1 of the ‘997 Patent further recites the step of “introducing triacetin and aqueous hydrogen peroxide to the water.”

43. The Accused Process also requires addition of hydrogen peroxide and triacetin. For example, the FSN states that, in Step 2 “hydrogen peroxide is blended into the mixture’s alkaline solution” and, in Step 3 “under continuous agitation, triacetin is added to the process.” (Exhibit G, pages 9-10; Figures 3-4).

44. Claim 1 of the ‘997 Patent further recites the step of “mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture.”

45. The FCN detailing the accused process states that “hydrogen peroxide is blended into the mixture’s alkaline solution” and “under continuous agitation,

triacetin is added to the process.” (Exhibit G, pages 9-10; Figures 3-4). The “blending” of hydrogen peroxide and addition of triacetin “under continuous agitation” necessarily forms a mixture of the ingredients.

46. Claim 1 of the ‘997 Patent further recites the step of “adding an aqueous source of an alkali metal or early alkali metal hydroxide to the mixture.”

47. The FCN also describes that the Accused Process includes the step of adding “concentrated sodium hydroxide providing an alkaline environment” to the water. (Exhibit G, page 9; Figure 1). Sodium hydroxide is most commonly used in chemical manufacturing as an aqueous solution and is an alkali metal hydroxide.

48. Claim 1 of the ‘997 Patent further recites the step of “forming a reaction medium comprising a non-equilibrium solution of peracetic acid.”

49. When the sodium hydroxide, hydrogen peroxide, and triacetin are all present in the water-based solution, the “[t]riacetin rapidly reacts with the alkaline peroxide to form an aqueous mixture of [peracetic acid],” (Exhibit G, page 10; Figure 5).

50. The Accused Process which first adds sodium hydroxide to water and subsequently adds hydrogen peroxide and triacetin is equivalent to “adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture.” The order in which the sodium hydroxide and the hydrogen peroxide and triacetin is insubstantial. First adding sodium hydroxide to water and then subsequently

adding hydrogen peroxide and triacetin is equivalent to “adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture” because it performs substantially the same function in substantially the same way to produce substantially the same result. Switching the order that sodium hydroxide is combined with hydrogen peroxide, triacetin, and water for reaction to form a non-equilibrium solution of peracetic acid will result in the sodium hydroxide performing substantially the same function in substantially the same way to produce substantially the same result.

C. The ‘443 Patent

51. The Accused Product includes all elements of, for example, claim 1 of the ‘443 Patent.

52. By way of example, claim 1 of the ‘443 Patent recites “[a] non-equilibrium solution of peracetic acid.”

53. The FCN states that “the [food contact substance] is prepared in a non-equilibrium process that produces PAA,” where PAA is defined to mean peracetic acid. (Exhibit G, page 9). The FCN therefore describes a method of forming a non-equilibrium peracetic acid.

54. Claim 1 of the ‘443 Patent further recites that the solution comprises “peracetic acid.”

55. When the sodium hydroxide, hydrogen peroxide, and triacetin are all present in the water-based solution, the “[t]riacetin rapidly reacts with the alkaline peroxide to form an aqueous mixture of [peracetic acid],” (Exhibit G, page 10; Figures 4-5). The resulting solution formed by the process described in the FCN includes peracetic acid.

56. Claim 1 of the ‘443 Patent further recites that the solution comprises “hydrogen peroxide.”

57. In formulating the Accused Product, “hydrogen peroxide is blended into the mixture[.]” (Exhibit G, page 9; Figure 4). The Accused Product, the resulting peracetic acid solution, therefore includes hydrogen peroxide because a chemical formulation comprises all of its reagents.

58. Claim 1 of the ‘443 Patent further recites that the solution comprises “triacetin.”

59. In formulating the Accused Product, “under continuous agitation, triacetin is added to the process.” (Exhibit G, page 9; Figure 4). The Accused Product, the resulting peracetic acid solution, therefore includes triacetin because a chemical formulation comprises all of its reagents.

60. Claim 1 of the ‘443 Patent further recites that the solution comprises “1,2,3-propanetriol.”

61. The FCN describes that, after the reaction between the sodium hydroxide, hydrogen peroxide, and triacetin are reacted, glycerol is a reaction product in the peracetic acid solution. (Exhibit G, page 10; Figure 4). The International Union of Pure and Applied Chemistry (IUPAC) name for glycerol is 1,2,3-propanetriol.

62. Claim 1 of the '443 Patent further recites that the solution comprises “an aqueous source of an alkali metal or earth alkali metal hydroxide.”

63. Formulating the Accused Product, as described in the FCN, includes the step of adding “concentrated sodium hydroxide providing an alkaline environment” to the solution. (Exhibit G, 9; Figure 4). the Accused Product, the resulting peracetic acid solution, therefore includes sodium hydroxide because a chemical formulation comprises all of its reagents.

64. Claim 1 of the '443 Patent further recites that the solution comprises “water.”

65. The Accused Product, manufactured according to the process described in the FCN, is “an aqueous mixture of [peracetic acid].” (Exhibit G, page 10). Water is inherent in an aqueous solution, and the first step of the FCN process is providing water as the basis for the reaction between the sodium hydroxide, hydrogen peroxide, and triacetin. (Exhibit G, page 9).

D. The '072 Patent

66. Defendant has directly infringed one or more claims of the '072 Patent, by intentionally developing, making, using, marketing, advertising, providing, sending, importing, distributing and/or selling the Accused Product.

67. The Accused Process includes all elements of, for example, claim 1 of the '072 Patent.

68. By way of example, claim 1 of the '072 Patent recites “[a] hydrogen peroxide-acetyl precursor solution.”

69. The FCN states that “the [food contact substance] is prepared in a non-equilibrium process that produces [peracetic acid].” (Exhibit G, page 9). In preparing the peracetic acid solution, the Accused Process necessarily includes formation of a hydrogen peroxide-acetyl precursor solution that ultimately reacts to form peracetic acid. (Exhibit G, pages 9-10).

70. Claim 1 of the '072 Patent further recites that the solution comprises “aqueous hydrogen peroxide.”

71. In formulating the hydrogen peroxide-acetyl precursor solution, the FCN states “hydrogen peroxide is blended into the mixer’s alkaline solution.” (Exhibit G, page 9). Hydrogen peroxide is most commonly used in chemical manufacturing in an aqueous form.

72. Claim 1 of the '072 Patent further recites that the solution comprises "triacetin."

73. In formulating the Accused Product, "under continuous agitation, triacetin is added to the process." (Exhibit G, page 9; Figure 4). The Accused Product, the resulting peracetic acid solution, therefore includes triacetin because a chemical formulation comprises all of its reagents.

74. Claim 1 of the '072 Patent further recites that the solution comprises "a trace amount of peracetic acid."

75. Upon mixing sodium hydroxide, hydrogen peroxide, and triacetin, "the reaction medium that is formed at this step almost instantly forms a non-equilibrium solution of [peracetic acid]." (Exhibit G, page 10). Because of the immediacy of the chemical reaction, the hydrogen peroxide-acetyl precursor solution necessarily includes at least trace amounts of peracetic acid.

76. Claim 1 of the '072 Patent further recites that the solution comprises "water."

77. The Accused Product, manufactured according to the process described in the FCN, is "an aqueous mixture of [peracetic acid]." (Exhibit G, page 10). Water is inherent in an aqueous solution, and the first step of the FCN process is providing water as the basis for the reaction between the sodium hydroxide, hydrogen peroxide, and triacetin. (Exhibit G, page 9).

COUNT I

Infringement of U.S. Patent No. 8,546,449

78. EnviroTech incorporates by reference each of the foregoing paragraphs as though fully set forth herein.

79. Defendant has infringed and is currently infringing, literally and/or under the doctrine of equivalents, the ‘449 Patent by, among other things, making, using, selling, offering for sale, and/or importing within this judicial district and elsewhere in the United States, without license or authority, products and/or processes that infringe one or more claims of the ‘449 Patent, including but not limited to the Accused Product and/or the Accused Process.

80. Upon information and belief, Defendant has had actual notice of its infringement of the ‘449 Patent since at least May 20, 2024, as evidenced by Exhibit E, but in any event, no later than the date of this Complaint.

81. Having actual notice of EnviroTech’s patent, the infringement by the Defendant of the ‘449 Patent continues to be willful and deliberate, and, therefore, EnviroTech is entitled to damages, including enhanced damages, under 35 U.S.C. § 284.

82. As a direct and proximate result of the infringement of the ‘449 Patent by Defendant, EnviroTech has suffered and will continue to suffer irreparable injury for which there is no adequate remedy at law. EnviroTech also has been

damaged and, until an injunction issues, will continue to be damaged in an amount yet to be determined.

COUNT II

Infringement of U.S. Patent No. 9,363,997

83. EnviroTech incorporates by reference each of the foregoing paragraphs as though fully set forth herein.

84. Defendant has infringed and is currently infringing, literally and/or under the doctrine of equivalents, the ‘997 Patent by, among other things, making, using, selling, offering for sale, and/or importing within this judicial district and elsewhere in the United States, without license or authority, products and/or processes that infringe one or more claims of the ‘997 Patent, including but not limited to the Accused Product and/or the Accused Process.

85. Upon information and belief, Defendant has had actual notice of its infringement of the ‘997 Patent since at least May 20, 2024, as evidenced by Exhibit E, but in any event, no later than the date of this Complaint.

86. Having actual notice of EnviroTech’s patent, the infringement by the Defendant of the ‘997 Patent continues to be willful and deliberate, and, therefore, EnviroTech is entitled to damages, including enhanced damages, under 35 U.S.C. § 284.

87. As a direct and proximate result of the infringement of the ‘997 Patent by Defendant, EnviroTech has suffered and will continue to suffer irreparable injury for which there is no adequate remedy at law. EnviroTech also has been damaged and, until an injunction issues, will continue to be damaged in an amount yet to be determined.

COUNT III

Infringement of U.S. Patent No. 9,730,443

88. EnviroTech incorporates by reference each of the foregoing paragraphs as though fully set forth herein.

89. Defendant has infringed and is currently infringing, literally and/or under the doctrine of equivalents, the ‘443 Patent by, among other things, making, using, selling, offering for sale, and/or importing within this judicial district and elsewhere in the United States, without license or authority, products and/or processes that infringe one or more claims of the ‘443 Patent, including but not limited to the Accused Product and/or the Accused Process.

90. Upon information and belief, Defendant has had actual notice of its infringement of the ‘443 Patent since at least May 20, 2024, as evidenced by Exhibit E, but in any event, no later than the date of this Complaint.

91. Having actual notice of EnviroTech’s patent, the infringement by the Defendant of the ‘443 Patent continues to be willful and deliberate, and, therefore,

EnviroTech is entitled to damages, including enhanced damages, under 35 U.S.C. § 284.

92. As a direct and proximate result of the infringement of the ‘443 Patent by Defendant, EnviroTech has suffered and will continue to suffer irreparable injury for which there is no adequate remedy at law. EnviroTech also has been damaged and, until an injunction issues, will continue to be damaged in an amount yet to be determined.

COUNT IV

Infringement of U.S. Patent No. 9,737,072

93. EnviroTech incorporates by reference each of the foregoing paragraphs as though fully set forth herein.

94. Defendant has infringed and is currently infringing, literally and/or under the doctrine of equivalents, the ‘072 Patent by, among other things, making, using, selling, offering for sale, and/or importing within this judicial district and elsewhere in the United States, without license or authority, products and/or processes that infringe one or more claims of the ‘072 Patent, including but not limited to the Accused Product and/or the Accused Process.

95. Upon information and belief, Defendant has had actual notice of its infringement of the ‘072 Patent since at least May 20, 2024, as evidenced by Exhibit E, but in any event, no later than the date of this Complaint.

96. Having actual notice of EnviroTech's patent, the infringement by the Defendant of the '072 Patent continues to be willful and deliberate, and, therefore, EnviroTech is entitled to damages, including enhanced damages, under 35 U.S.C. § 284.

97. As a direct and proximate result of the infringement of the '072 Patent by Defendant, EnviroTech has suffered and will continue to suffer irreparable injury for which there is no adequate remedy at law. EnviroTech also has been damaged and, until an injunction issues, will continue to be damaged in an amount yet to be determined.

JURY DEMAND

EnviroTech requests a jury trial on all issues so triable.

PRAYER FOR RELIEF

WHEREFORE, EnviroTech requests that the Court enter the following in its favor and against Defendant as follows:

- A. A judgment in favor of EnviroTech on all of its claims against Defendant;
- B. A judgment that Defendant has violated 35 U.S.C. § 271 by infringing, directly or indirectly, and literally, or under the doctrine of equivalents,

one or more claims of the '449 Patent, the '997 Patent, the '180 Patent, the '443 Patent, and the '072 Patent.

C. A judgment awarding EnviroTech damages adequate to compensate for Defendant's infringement, but in no event less than a reasonable royalty under 35 U.S.C. § 284, in an amount to be determined at trial;

D. A judgment that Defendant's patent infringement has been and continues to be willful, and a trebling of damages pursuant to 35 U.S.C. § 284;

E. A judgment declaring that this is an exceptional case and awarding EnviroTech its actual costs, expenses, and reasonable attorneys' fees under 35 U.S.C. § 285;

F. A judgment that Defendant and its respective officers, agents, servants, employees, and attorneys, and all other persons who are in active concert or participation with them are enjoined, preliminarily and permanently, from further infringement of the '449 Patent, the '997 Patent, the '180 Patent, the '443 Patent, the '072 Patent, and the '230 Patent;

G. A judgment awarding EnviroTech pre-judgment and post-judgment interest; and

H. A judgment awarding such further, equitable or other relief as the Court deems just and proper.

Dated: October 29, 2024

Respectfully submitted,

EVERSHEDS SUTHERLAND (US) LLP

/s/ Michael J. Woodson

Michael J. Woodson

Texas State Bar No. 24084117

98 San Jacinto Blvd, Suite 1600

Austin, Texas 78701

Telephone: 512.721.2770

Facsimile: 713.654.1301

michaelwoodson@eversheds-sutherland.com

Ann G. Fort (*pro hac vice forthcoming*)

Georgia State Bar No. 269995

Lindsay M. Kriz (*pro hac vice forthcoming*)

Georgia State Bar No. 624085

999 Peachtree Street, NE, Suite 2300

Atlanta, Georgia 30309

Telephone: 404.853.8000

Facsimile: 404.853.8806

annfort@eversheds-sutherland.com

lindsaykriz@eversheds-sutherland.com

***Attorneys for Plaintiff EnviroTech
Chemical Services, Inc.***

EXHIBIT A



US008546449B2

(12) **United States Patent**
Harvey et al.

(10) **Patent No.:** **US 8,546,449 B2**
(45) **Date of Patent:** **Oct. 1, 2013**

(54) **METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE**

2010/0196505 A1 8/2010 Kaiser
2010/0227000 A1 9/2010 Ames et al.
2012/0165407 A1 6/2012 Gupta
2012/0172441 A1 7/2012 Li

(75) Inventors: **Michael S. Harvey**, Modesto, CA (US);
Jonathan N. Howarth, Modesto, CA (US)

FOREIGN PATENT DOCUMENTS

EP 0 563 460 B1 7/1998
WO WO 01/46519 A1 6/2001
WO WO 2008/140988 A1 11/2008
WO WO 2010/005607 A2 1/2010

(73) Assignee: **Enviro Tech Chemical Services, Inc.**, Modesto, CA (US)

OTHER PUBLICATIONS

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 162 days.

Leveneur, et al., "Interaction of Intrinsic Kinetics and Internal Mass ... Acids," Chemical Engineering Science 64 (2009) pp. 4101-4114.
Rocha, et al., "Rates of Formation of Peroxyacetic ... Phosphates," Journal of Molecular Catalysis A: Chemical 186 (2002) pp. 127-133.
Clariant Corp., technical bulletin, "Peractive—The Clean and Clever Way of Bleaching," Aug. 1999.
Milne, "Oxygen Bleaching Systems in Domestic Laundry," Journal of Surfactants and Detergents, vol. 1, No. 2 (Apr. 1998) pp. 253-261.
Saha, et al., "Synthesis of Peroxyacetic Acid Using in Situ ... Electrode," Electrochemistry Communications 5 (2003) pp. 445-448.

(21) Appl. No.: **13/065,553**

(22) Filed: **Mar. 24, 2011**

(65) Prior Publication Data

US 2012/0245228 A1 Sep. 27, 2012

* cited by examiner

(51) **Int. Cl.**
A61K 31/19 (2006.01)

(52) **U.S. Cl.**
USPC **514/557**

(58) **Field of Classification Search**
USPC 514/557
See application file for complete search history.

Primary Examiner — Rei-tsang Shiao

(74) *Attorney, Agent, or Firm* — Audrey A. Millemann; Weintraub Tobin

(56) References Cited

U.S. PATENT DOCUMENTS

3,432,546 A 3/1969 Oringer et al.
3,956,159 A 5/1976 Jones
5,122,538 A 6/1992 Lokkesmoe et al.
5,977,403 A 11/1999 Byers
6,171,551 B1 1/2001 Malchesky et al.
6,262,013 B1 7/2001 Smith et al.
6,387,236 B2 5/2002 Nordman et al.
7,012,154 B2 3/2006 Vineyard et al.
7,271,137 B2 9/2007 Tucker et al.
7,723,083 B2 5/2010 DiCosimo et al.
7,919,122 B2 4/2011 Okano et al.
2004/0245116 A1 12/2004 Ohsaka et al.
2005/0118940 A1 6/2005 Hilgren et al.
2007/0082832 A1* 4/2007 DiCosimo et al. 510/305
2009/0043123 A1 2/2009 Copenhafer et al.
2009/0175956 A1 7/2009 Buschmann et al.
2009/0314652 A1 12/2009 Buschmann et al.

(57) ABSTRACT

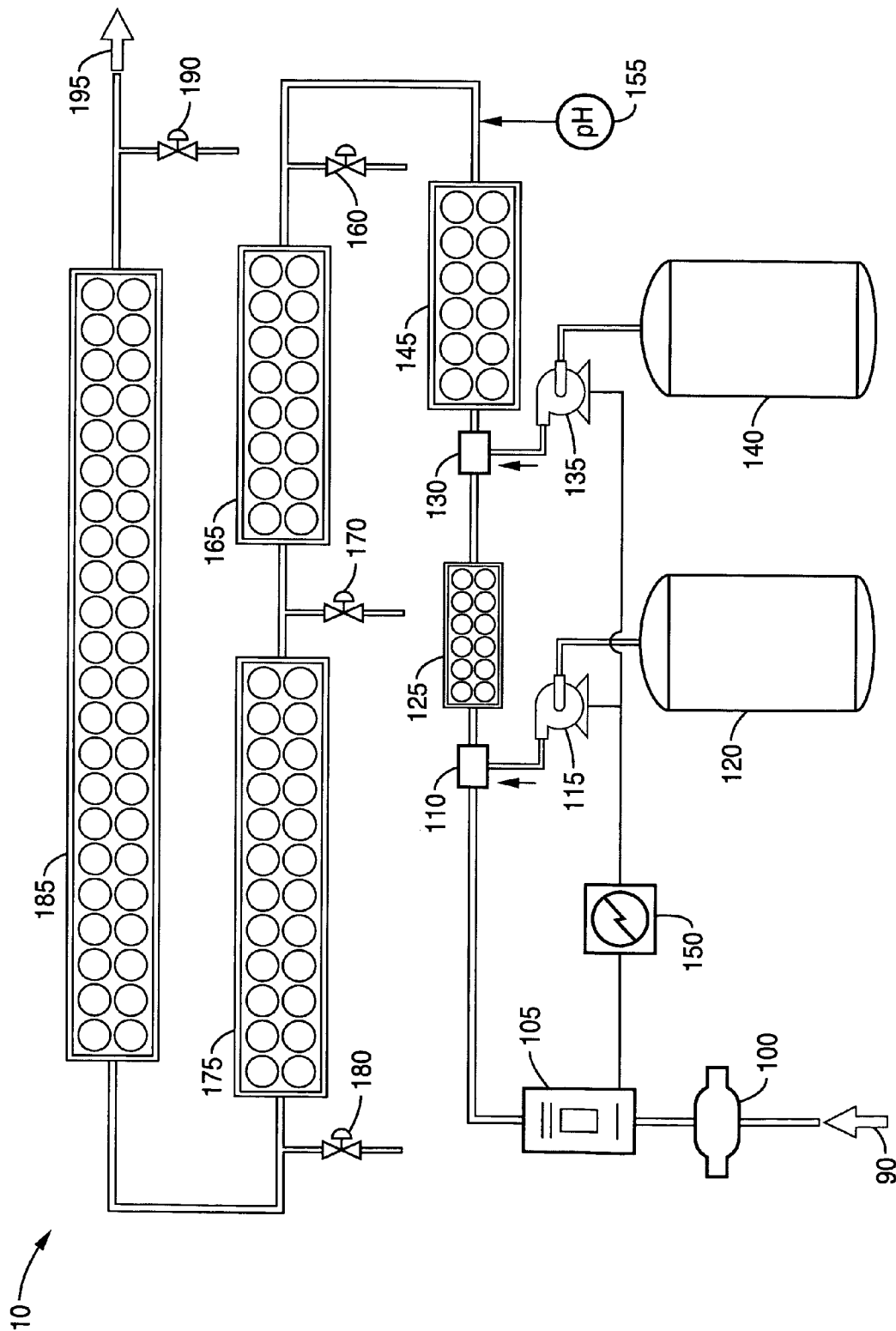
Methods and compositions for the generation of a peroxyacetic acid sanitizer in proximity to the point-of-use are disclosed. These methods comprise introducing a hydrogen peroxide-acetyl precursor solution to water, mixing, and then adding an aqueous source of an alkali metal or earth alkali metal hydroxide. 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.

23 Claims, 1 Drawing Sheet

U.S. Patent

Oct. 1, 2013

US 8,546,449 B2



US 8,546,449 B2

1

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

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

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 bio-film removal in papermaking processes.

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

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

2

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.

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. Pat. 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.

Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. Pat. 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.

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 com-

US 8,546,449 B2

3

partment. 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.

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).

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. Pat. 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.

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. Pat. 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

4

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.

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.

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 tetraacetylenediamine (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.

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

B. Solid PAA Bleaches and Stain Removers

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, tetraacetylenediamine (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

US 8,546,449 B2

5

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

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.

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

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.

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,

6

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.

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%.

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.

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 perhydrolyase 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.

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.

US 8,546,449 B2

7

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.

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.

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

FIG. 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point-of-use of peracetic acid. In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

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

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

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

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

2. Experimental Methods

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:

8

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

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

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.

In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. Pat. 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 ($76/71=1.07$).

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

3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA On a Site Having a Point-of-Use

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.

The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

- (a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.

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.,

US 8,546,449 B2

9

triacetin is unexpectedly highly soluble in 50% hydrogen peroxide. It solubilizes without an exotherm (temperature increase).

The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

(b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

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.

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.

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.

The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

EXAMPLE 1

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.

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.

In order to test the stability of the mixture, the amount of hydrogen peroxide remaining and the amount of PAA gener-

10

ated was tracked for several months. The mixture was held at ambient temperature away from sources of light. Table I summarizes the data.

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

Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

EXAMPLE 2

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.

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

Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

EXAMPLE 3

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

US 8,546,449 B2

11

and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

TABLE III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

EXAMPLE 4

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 W shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

TABLE IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

EXAMPLE 5

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.

12

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

Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

EXAMPLE 6

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.

TABLE VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.

EXAMPLE 7

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.

US 8,546,449 B2

13

After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate-iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.

TABLE VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

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

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.

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

(a) Providing water.

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

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.

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

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

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.

14

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

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

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 $\frac{3}{4}$ " pipe, a static mixer of $\frac{3}{4}$ " diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

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

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.

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.

US 8,546,449 B2

15

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.

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.

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

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

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.

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).

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

16

reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

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

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

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.

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

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

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

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

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.

Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28%

US 8,546,449 B2

17

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.

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.

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

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

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.

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).

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:



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 perhydrolysis 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).

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%.

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.

18

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.

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.

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

EXAMPLE 8

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.

TABLE VIII

Test #	Moles		pH of Buffer	Hydrogen Peroxide Used (Wt., g)	Triacetin Used (Wt., g)	% PAA Generated	% Hydrogen Peroxide Remaining		% Triacetin Converted to PAA
	Hydrogen Peroxide/ Mole Triacetin	Type of Addition (Double, Sequential or Mixed)					Hydrogen Peroxide		
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%

US 8,546,449 B2

19

20

TABLE VIII-continued

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 Remaining	% Triacetin Converted to PAA
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%

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

EXAMPLE 9

A mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (63.4%) and triacetin (36.6%). Thus, the mole ratio of hydrogen peroxide:triacetin was 5.57:1. The mixture (13.68 g) was added to soft water such that the final solution contained 5 g/L of triacetin and had a pH of 4.1. Then, in successive experiments, sufficient 50% NaOH was added to the beaker so that the mole ratio of NaOH:TA was varied from 3:1 (obtained by introducing 5.49 g of 50% NaOH) to 8:1 (obtained by introducing 14.68 g of 50% NaOH). Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the 6:1 mole ratio of NaOH:TA are shown in Table IX.

TABLE IX

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
0	0.015	0.437	2.9
1	0.275	0.298	53.1

TABLE IX-continued

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
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

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.

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.

US 8,546,449 B2

21

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

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.

EXAMPLE 10

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

TABLE XI

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

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.

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.

22

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

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

EXAMPLE 11

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

TABLE XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.247	0.207	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

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.

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.

US 8,546,449 B2

23

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

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

EXAMPLE 12

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.

In the second test, the first test was repeated, except that the water was chilled soft water.

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.

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.

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

24

maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

TABLE XV

Test #	Initial Temp. (° F.)	Final Temp. (° F.)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

TABLE XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

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.

EXAMPLE 13

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.

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.

US 8,546,449 B2

25

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.

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.

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.

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

26

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.

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**.

Point-of-use **195** may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products; fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

EXAMPLE 14

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.

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**.

The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate-iodometric titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

TABLE XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide-Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	~13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37
4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

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

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

US 8,546,449 B2

27

peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

EXAMPLE 15

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.

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.

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.

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, Calif.). 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.

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.

All 3M *E. coli* Petrifilms and 3M Enterobacteriaceae Petrifilms were incubated at 35° C. for 24 hours. After incubation, the plates were enumerated.

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 log₁₀ 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.

28

The *E. coli* test solution treated with 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 6.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log₁₀ 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 log₁₀ 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.

TABLE XVIII

<i>E. coli</i> 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

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 log₁₀ 7.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.

The *Salmonella* solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 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 log₁₀ 6.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log₁₀ 4.95 CFU/mL remained (99.24% reduction).

TABLE XIX

<i>Salmonella typhimurium</i>			
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

The data in tables XVIII and XIX demonstrate that the 1% PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%, about equal to that of the Perasan MP-2, which was >99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

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,

US 8,546,449 B2

29

borate, silicate, or hydroxide. Examples include sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, sodium borate, sodium borate decahydrate (borax), sodium metasilicate, and sodium hydroxide.

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.

The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispersency, and lower surface tension.

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.

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.

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.

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.

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 surfactant, 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 homogenous mixture. The mixture is a freely-flowable solid which is readily discharged from the blender.

EXAMPLE 16

A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non-flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.

TABLE XX

Component	%
Sodium carbonate, anhydrous	26.3
Sodium percarbonate	58.9

30

TABLE XX-continued

Component	%
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

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 9.1 g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

TABLE XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely-flowable solid	None
2	Freely-flowable solid	None
3	Freely-flowable solid	None
4	Freely-flowable solid	None
5	Freely-flowable solid	None
6	Freely-flowable solid	None
7	Freely-flowable solid	None
8	Freely-flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45 g 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.

The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.

TABLE XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

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.

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

US 8,546,449 B2

31

was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

EXAMPLE 17

Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.

TABLE XXIII

	%	Charge Weights, g
Components of Composition A		
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		
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

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.

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.

Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

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.

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.

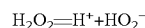
32

The solid peroxygen bleaching and stain removal composition described above may be used as follows.

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 5 g 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.

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.

While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:



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.

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.

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.

Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

EXAMPLE 18

Laundry swatches were made by cutting a tea towel into 50 equal 5×4 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.

A solid peroxygen bleaching and stain removal composition (200 g) was prepared by blending sodium percarbonate

US 8,546,449 B2

33

(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.

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. Pat. No. 7,651,724. At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75° F., the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104° F. had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H₂O₂). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75° F. at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104° F. at a pH of 11.2.

TABLE XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

TABLE XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426
5.5	133	1494
7.8	122	1427
10.3	119	1405

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.).

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.

34

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

The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

TABLE XXVII

Type of Stain	Bleaching Formula at 64° F.	Bleaching Formula at 120° F.
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

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.

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.

We claim:

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

- providing water;
- introducing a hydrogen peroxide-triacetin solution to the water;
- mixing the hydrogen peroxide-triacetin solution and the water to form a mixture;
- adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and
- forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

2. The method of claim 1, further comprising, prior to step (b), a step of providing the hydrogen peroxide-triacetin solution comprising: introducing triacetin to a solution of aqueous hydrogen peroxide; and allowing the triacetin and the solution of aqueous hydrogen peroxide to mix to form the hydrogen peroxide-triacetin solution.

3. The method of claim 1, 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.

US 8,546,449 B2

35

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

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

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

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

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

9. The method of claim 1, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide triacetin into peracetic acid.

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

11. The method of claim 10, further comprising, after step (e), a step of sampling the reaction medium to determine the time required to maximize the amount of hydrogen peroxide triacetin that are converted into peracetic acid.

12. The method of claim 9, wherein and the percent of triacetin that is converted into peracetic acid is about 40.9% to about 85.7%.

13. The method of claim 7, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

36

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

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

16. The method of claim 1, wherein the peracetic acid solution is for immediate use.

17. The method of claim 1, 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.

18. The method of claim 1, wherein the peracetic acid solution is prepared on a site having a point-of-use.

19. The method of claim 2, wherein the liquid is triacetin defining a hydrogen peroxide-triacetin solution.

20. The method of claim 19, 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.

21. The method of claim 19, wherein the aqueous source of the alkali metal or earth alkali metal hydroxide is sodium hydroxide.

22. The method of claim 21, wherein the sodium hydroxide is about 1.82% to about 7.28%.

23. The method of claim 22, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:18:1.

* * * * *

EXHIBIT B



US009363997B2

(12) **United States Patent**
Harvey et al.

(10) **Patent No.:** **US 9,363,997 B2**
(45) **Date of Patent:** ***Jun. 14, 2016**

(54) **METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE**

(71) Applicants: **Michael S. Harvey**, Modesto, CA (US);
Jonathan N. Howarth, Modesto, CA (US)

(72) Inventors: **Michael S. Harvey**, Modesto, CA (US);
Jonathan N. Howarth, Modesto, CA (US)

(73) Assignee: **Enviro Tech Chemical Services, Inc.**,
Modesto, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/681,938**

(22) Filed: **Apr. 8, 2015**

(65) **Prior Publication Data**

US 2015/0208652 A1 Jul. 30, 2015

Related U.S. Application Data

(62) Division of application No. 14/019,296, filed on Sep. 5, 2013, which is a division of application No. 13/065,553, filed on Mar. 24, 2011, now Pat. No. 8,546,449.

(51) **Int. Cl.**
A61K 31/19 (2006.01)
A01N 37/16 (2006.01)

C11D 3/39 (2006.01)

C11D 11/00 (2006.01)

A01N 59/00 (2006.01)

C11D 3/395 (2006.01)

D06L 3/02 (2006.01)

(52) **U.S. Cl.**

CPC **A01N 37/16** (2013.01); **A01N 59/00** (2013.01); **C11D 3/3947** (2013.01); **C11D 3/3955** (2013.01); **C11D 3/3956** (2013.01); **C11D 11/0041** (2013.01); **D06L 3/025** (2013.01)

(58) **Field of Classification Search**

USPC 514/557
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

8,546,449 B2 * 10/2013 Harvey C11D 3/3947
514/557

* cited by examiner

Primary Examiner — Rei-Tsang Shiao

(74) *Attorney, Agent, or Firm* — Audrey A. Millemann;
Weintraub Tobin

(57) **ABSTRACT**

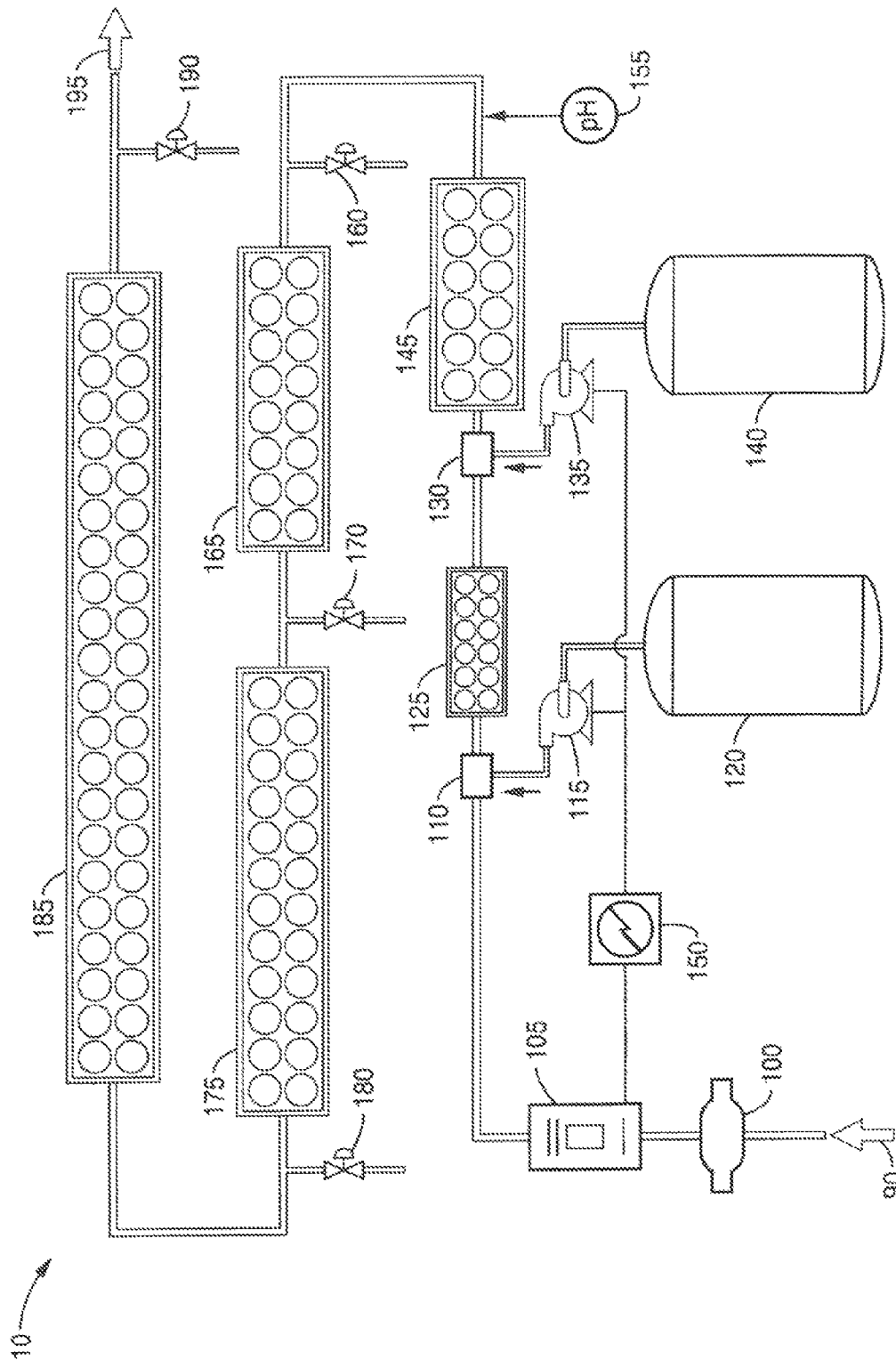
Methods for the generation of non-equilibrium solutions of peroxyacetic acid are disclosed. These methods comprise introducing triacetin sad aqueous hydrogen peroxide to water, mixing, and then adding an aqueous source of an alkali metal or earth alkali metal hydroxide. Triacetin is converted rapidly and with a high conversion rate into peracetic acid. These methods produce solutions with a high level of peracetic acid.

14 Claims, 1 Drawing Sheet

U.S. Patent

Jun. 14, 2016

US 9,363,997 B2



US 9,363,997 B2

1

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

CROSS REFERENCE TO RELATED APPLICATIONS

This is a divisional application of co-pending U.S. patent application Ser. No. 14/019,296 filed on Sep. 5, 2013, which is a divisional of prior application Ser. No. 13/065,553 filed on Mar. 24, 2011, now U.S. Pat. No. 8,546,449 issued on Oct. 1, 2013, pursuant to 35 U.S.C. §§120 and 121, and hereby incorporates both applications by reference in their entirety.

FIELD OF INVENTION

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.

A. Liquid PAA Disinfectants and Sanitizers

This is a divisional of prior application Ser. No. 14/019,296 filed on Sep. 5, 2013. 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.

Peroxyacetic acid products are supplied as stable equilibrium ternary aqueous solutions of peroxyacetic acid, acetic acid, and hydrogen peroxide. They are prepared in advance of delivery, typically by reacting hydrogen peroxide with acetic acid in the presence of a mineral acid catalyst. Although some PAA is formed immediately, the PAA does not reach its maximum concentration until after several days. A metal chelating agent, such as hydroxyethylidene diphosphonic acid (HEDP) or dipicolinic acid, is also introduced to suppress the transition metal cation catalyzed decomposition of peroxygen compounds. The PAA product is then placed in containers, such as totes, drums and pads, 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.

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 perox-

2

ide 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.

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. Pat. 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.

Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. Pat. No. 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.

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

US 9,363,997 B2

3

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.

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).

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. Pat. 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.

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. Pat. No. 3,432,546 discloses a process where hydrogen peroxide, acetic anhydride, and an ammonium

4

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 acid in the treatment of meat, poultry, and seafood.

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.

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 tetraacetylenediamine (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.

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

B. Solid PAA Bleaches and Stain Removers

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, tetraacetylenediamine (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

US 9,363,997 B2

5

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 tile 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

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.

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

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.

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

6

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.

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%.

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.

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 perhydrolyase 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.

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,

US 9,363,997 B2

7

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.

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.

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.

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

FIG. 1 is a schematic representation of an example of a system that, may be used to continuously or intermittently generate PAA for on a site having a point-of-use of peracetic acid. In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

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

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

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

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

2. Experimental Methods

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 ferrous 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,

8

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:

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

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

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.

In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. Pat. 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 ($76/71=1.07$).

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 tire colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl_2 . After subtracting the ppm reading obtained earlier for the contribution due to PAA, a calculation is then used to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2 ($34/71=0.479$).

3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA on a Site Having a Point-of-Use

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.

The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

- (a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.

US 9,363,997 B2

9

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).

The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

(b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

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.

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.

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.

The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

Example 1

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.

10

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.

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.

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

Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

Example 2

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.

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

Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

Example 3

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin

US 9,363,997 B2

11

(37.5008 g) to 50% hydrogen peroxide 165.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

TABLE III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

Example 4

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

TABLE IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

Example 5

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.

12

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

Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

Example 6

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.

TABLE VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11 % PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.

Example 7

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.

After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric Sulfate-iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.

TABLE VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

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

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.

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

(a) Providing water.

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

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.

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

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

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.

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

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

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 $\frac{3}{4}$ " pipe, a static mixer of $\frac{3}{4}$ " diameter and 6" long, and a velocity of about 1 gal/mm., mixing should be accomplished in less than about one second.

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

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.

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.

US 9,363,997 B2

15

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.

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.

Step (d) may be performed after step (e), or it may be performed simultaneously with step (b).

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

The reaction median 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.

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).

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 tire 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

16

reaction medium is directed through the sampling point of maximum conversion of acetyl precursor and to the point-of-use.

In another embodiment, a method of continuously or intermittently generating a Non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing water.

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

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

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.

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

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

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

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

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.

Sufficient 50% NaOH is added to the mixture such that the amount of sodium hydroxide is about 1.82% to about 7.28%

US 9,363,997 B2

17

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.

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.

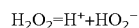
Step (d) may be performed alter step (c), or it may be performed simultaneously with step (b).

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

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.

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).

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:



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 perhydrolysis 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).

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%.

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.

18

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.

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.

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

Example 8

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.

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 Remaining	% 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%

TABLE VIII-continued

Test #	Moles		pH of Buffer	Hydrogen Peroxide		% PAA Generated	% Hydrogen Peroxide		% Triacetin Converted to PAA
	Hydrogen Peroxide/ Triacetin	Type of Addition (Double Sequential or Mixed)		Used (Wt., g)	Triacetin Used (Wt., g)		Remaining	Triacetin	
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	25.5	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%	
31	16.0	Mixed	10.97	0.595	0.119	0.00035	0.018	2.8%	

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

Example 9

A mixture of triacetin and hydrogen peroxide was prepared by blending 50% hydrogen peroxide (63.4%) and triacetin (36.0%). 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 5.40 g of 50% NaOH) to 8:1 (obtained by introducing 14.68 g of 50% NaOH). Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured over the next 20 minutes. The method was performed in duplicate for each sample point. The averages of the results for the 6:1 mole ratio of NaOH:TA are shown in Table IX.

TABLE IX

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
0	0.015	0.437	2.9
1	0.275	0.298	53.1
3	0.312	0.274	60.2
5	0.326	0.258	62.9
11	0.302	0.233	58.3
21	0.246	0.199	47.5

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.

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.

US 9,363,997 B2

21

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

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.

Example 10

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

TABLE XI

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

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.

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.

22

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

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

Example 11

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

TABLE XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.247	0.207	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

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.

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.

US 9,363,997 B2

23

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

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

Example 12

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.

In the second test, the first test was repeated except that the water was chilled soft water.

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.

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.

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

24

maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

TABLE XV

Test #	Initial Temp. (° F.)	Final Temp. (° F.)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

TABLE XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

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.

Example 13

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.

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.

US 9,363,997 B2

25

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.

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.

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.

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 resi-

26

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.

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**.

Point-of-use **195** may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products; fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

Example 14

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.

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**.

The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate-iodometric titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

TABLE XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide-Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	~13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37
4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

dence 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

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

US 9,363,997 B2

27

generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

Example 15

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.

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.

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.

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, Calif.). 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*, respectively.

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.

All 3M *E. coli* Petrifilms and 3M *Enterobacteriaceae* Petrifilms were incubated at 35° C. for 24 hours. After incubation, the plates were enumerated.

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 log₁₀ 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.

28

The *E. coli* test solution treated with 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 6.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log₁₀ 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 log₁₀ 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.

TABLE XVIII

<i>E. coli</i> 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

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 log₁₀ 7.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.

The *Salmonella* solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 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 log₁₀ 6.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log₁₀ 4.95 CFU/mL remained (99.24% reduction).

TABLE XIX

<i>Salmonella typhimurium</i>			
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

The data in tables XVIII and XIX demonstrate that the 1% PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%, about equal to that of the Perasan MP-2, which was >99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

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,

US 9,363,997 B2

29

borate, silicate, or hydroxide. Examples include sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, sodium borate, sodium borate decahydrate (borax), sodium metasilicate, and sodium hydroxide.

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.

The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispersency, and lower surface tension.

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.

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.

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.

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.

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 surfactant, 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 homogenous mixture. The mixture is a freely-flowable solid which is readily discharged from the blender.

Example 16

A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non-flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.

TABLE XX

Component	%
Sodium carbonate, anhydrous	26.3
Sodium percarbonate	58.9

30

TABLE XX-continued

Component	%
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

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 9.1 g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

TABLE XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely-flowable solid	None
2	Freely-flowable solid	None
3	Freely-flowable solid	None
4	Freely-flowable solid	None
5	Freely-flowable solid	None
6	Freely-flowable solid	None
7	Freely-flowable solid	None
8	Freely-flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45 g 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.

The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.

TABLE XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

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.

These surprising results are in contest 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

US 9,363,997 B2

31

was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

Example 17

Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.

TABLE XXIII

	%	Charge Weights, g
Components of Composition A		
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		
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

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.

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.

Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

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.

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.

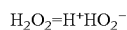
32

The solid peroxygen bleaching and stain removal composition described above may be used as follows.

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 5 g 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.

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.

While not wishing, to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:



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.

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.

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.

Fifth the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

Example 18

Laundry swatches were made by cutting a tea towel into 50 equal 5×4 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 (park), 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.

A solid peroxygen bleaching and stain removal composition (200 g) was prepared by blending sodium percarbonate

US 9,363,997 B2

33

(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.

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. Pat. No. 7,651,724. At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75° F., the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104° F. had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H₂O₂). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75° F. at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104° F. at a pH of 11.2.

TABLE XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

TABLE XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426
5.5	133	1494
7.8	122	1427
10.3	119	1405

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.).

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.

34

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

The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated, the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

TABLE XXVII

Type of Stain	Bleaching Formula at 64° F.	Bleaching Formula at 120° F.
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

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.

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.

We claim:

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

- providing water;
- introducing triacetin and aqueous hydrogen peroxide to the water;
- mixing the triacetin and the aqueous hydrogen peroxide with the water to form a mixture;
- adding an aqueous source of an alkali metal or earth alkali metal hydroxide to the mixture; and
- forming a reaction medium comprising a non-equilibrium solution of peracetic acid.

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

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

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

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

US 9,363,997 B2

35

36

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

7. The method of claim 6, wherein, the sodium hydroxide is about 1.82% to about 7.28%. 5

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

9. The method of claim 1, further comprising allowing the reaction medium sufficient time to maximize the conversion of the hydrogen peroxide and the triacetin into peracetic acid. 10

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

11. The method of claim 10, wherein the percent of triacetin that is converted into peracetic acid is about 40.9% to 15 about 85.7%.

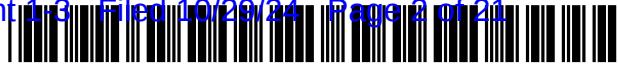
12. The method of claim 6, wherein the mole ratio of the sodium hydroxide to the hydrogen peroxide to the triacetin is about 4.2:3.8:1.

13. The method of claim 1, wherein said steps (a) through 20 (e) are performed on a continuous basis.

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

* * * * *

EXHIBIT C



US009730443B2

(12) **United States Patent**
Harvey et al.

(10) **Patent No.:** **US 9,730,443 B2**

(45) **Date of Patent:** ***Aug. 15, 2017**

(54) **METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE**

A01N 59/00 (2006.01)

C11D 3/395 (2006.01)

A01N 37/12 (2006.01)

B01J 19/24 (2006.01)

D06L 4/15 (2017.01)

(71) Applicant: **Enviro Tech Chemical Services, Inc.**,
Modesto, CA (US)

(72) Inventors: **Michael S. Harvey**, Modesto, CA (US);
Jonathan N. Howarth, Modesto, CA (US)

(73) Assignee: **Enviro Tech Chemical Services, Inc.**,
Modesto, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/063,306**

(22) Filed: **Mar. 7, 2016**

(65) **Prior Publication Data**

US 2016/0183523 A1 Jun. 30, 2016

Related U.S. Application Data

(62) Division of application No. 14/019,296, filed on Sep. 5, 2013, now Pat. No. 9,370,180, which is a division of application No. 13/065,553, filed on Mar. 24, 2011, now Pat. No. 8,546,449.

(51) **Int. Cl.**

A61K 31/19 (2006.01)

A01N 37/16 (2006.01)

C11D 3/39 (2006.01)

C11D 11/00 (2006.01)

(52) **U.S. Cl.**

CPC *A01N 37/16* (2013.01); *A01N 37/12*

(2013.01); *A01N 59/00* (2013.01); *B01J 19/24*

(2013.01); *C11D 3/3947* (2013.01); *C11D*

3/3955 (2013.01); *C11D 3/3956* (2013.01);

C11D 11/0041 (2013.01); *D06L 4/15*

(2017.01); *B01J 2219/24* (2013.01)

(58) **Field of Classification Search**

USPC 514/557

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2016/0183531 A1* 6/2016 Harvey C11D 3/3947
424/616

* cited by examiner

Primary Examiner — Rei-Tsang Shiao

(74) *Attorney, Agent, or Firm* — Audrey A. Millemann;
Weintraub Tobin

(57) **ABSTRACT**

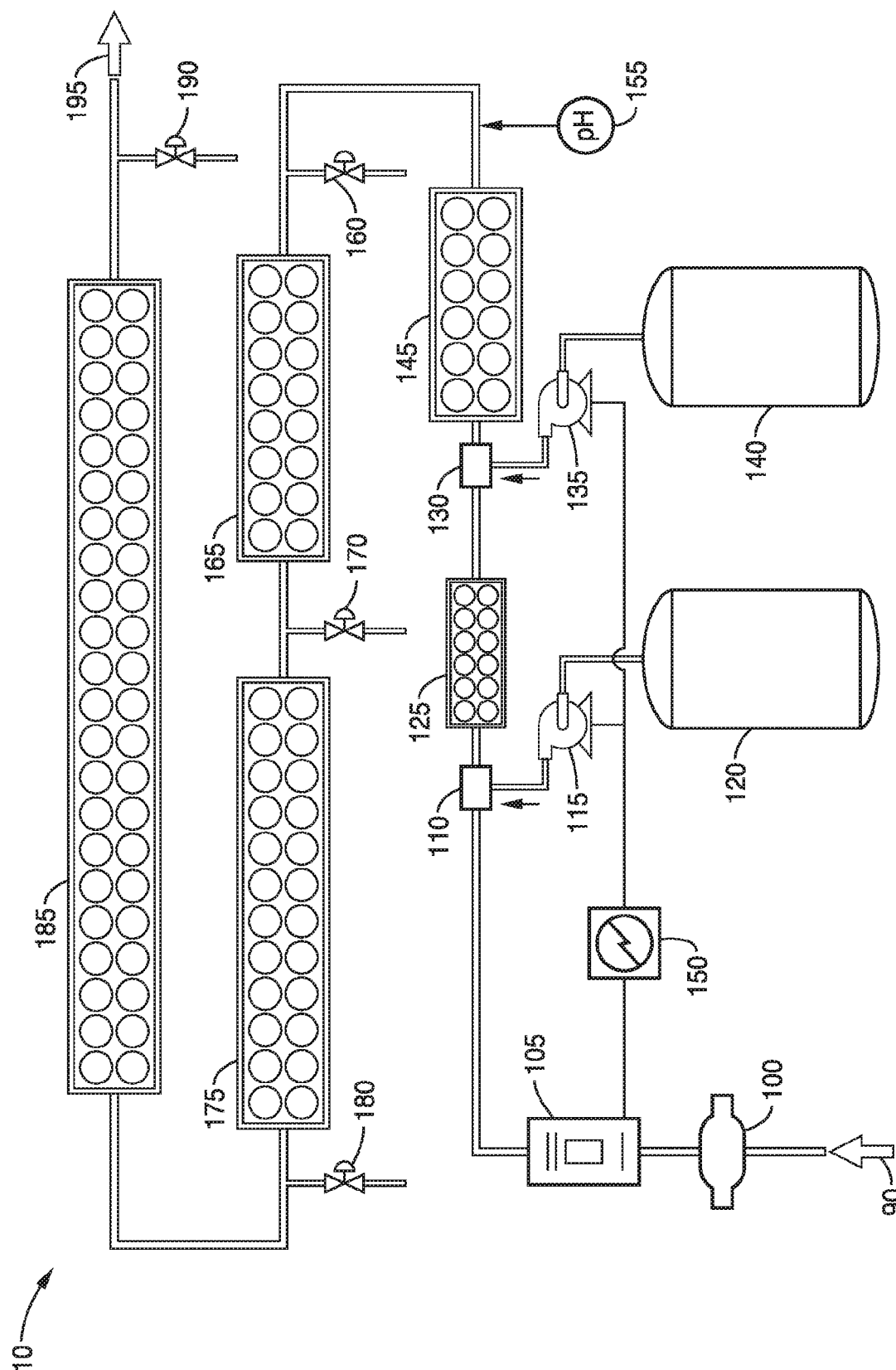
Methods for the generation of non-equilibrium solutions of peroxyacetic acid are disclosed. These methods comprise introducing triacetin and aqueous hydrogen peroxide to water, mixing, and then adding an aqueous source of an alkali metal or earth alkali metal hydroxide. Triacetin is converted rapidly and with a high conversion rate into peracetic acid. These methods produce solutions with a high level of peracetic acid.

3 Claims, 1 Drawing Sheet

U.S. Patent

Aug. 15, 2017

US 9,730,443 B2



US 9,730,443 B2

1

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

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a divisional application of U.S. patent application Ser. No. 14/019,296 filed on Sep. 5, 2013, which is a divisional of prior application Ser. No. 13/065,553 filed on Mar. 24, 2011, now U.S. Pat. No. 8,546,449 issued on Oct. 1, 2013, pursuant to 35 U.S.C. §§120 and 121, and hereby incorporates both applications by reference in their entirety.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

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.

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

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

2

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.

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. Pat. 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.

Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. Pat. 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.

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, where-

US 9,730,443 B2

3

upon 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.

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).

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. Pat. 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.

4

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. Pat. 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.

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 side-stream 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.

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 tetraacetylenediamine (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.

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

B. Solid PAA Bleaches and Stain Removers

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, tetraacetylenediamine (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

US 9,730,443 B2

5

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

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.

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

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.

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

6

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.

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%.

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.

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

US 9,730,443 B2

7

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.

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.

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.

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.

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

FIG. 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point-of-use of peracetic acid. In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

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

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

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

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

8

2. Experimental Methods

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:

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

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

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.

In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. Pat. 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 ($76/71=1.07$).

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

US 9,730,443 B2

9

to convert this number into ppm as hydrogen peroxide, and is based on the weight ratio of hydrogen peroxide to Cl_2 ($34/71=0.479$).

3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA on a Site Having a Point-of-Use

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.

The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

- (a) Introducing a liquid acetyl precursor that is soluble in aqueous hydrogen peroxide to a solution of aqueous hydrogen peroxide.

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).

The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

- (b) Allowing the acetyl precursor and the aqueous hydrogen peroxide to mix to form a hydrogen peroxide-acetyl precursor solution.

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.

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.

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.

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

10

transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

Example 1

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.

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.

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.

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

Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

Example 2

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.

US 9,730,443 B2

11

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

Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

Example 3

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin (37.5008 g) to 50% hydrogen peroxide (65.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

TABLE III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

Example 4

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

TABLE IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1

12

TABLE IV-continued

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
15	24.17	1.17
22	23.68	1.14

Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

Example 5

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 4.8:1 was prepared by adding triacetin (37.50 g) to 50% hydrogen peroxide (56.25 g) so that the mixture was 30% hydrogen peroxide and 40% triacetin, with the balance being water. The pH of the solution was 1.67 and the pH of a 1:100 dilution was 4.62. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table V shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 43 days.

TABLE V

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	30.08	0.38
8	29.85	0.784
15	29.63	1.22
22	29.37	1.71
29	28.76	2.26
36	28.67	2.78
43	28.31	3.41

Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

Example 6

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.

US 9,730,443 B2

13

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

Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.

Example 7

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.

After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate-iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.

TABLE VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

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.

14

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

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.

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

(a) Providing Water.

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

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.

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

(b) Introducing a Hydrogen Peroxide-Acetyl Precursor Solution to the Water.

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.

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

US 9,730,443 B2

15

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

(c) Mixing the Hydrogen Peroxide-Acetyl Precursor Solution and the Water to Form a Mixture.

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 $\frac{3}{4}$ " pipe, a static mixer of $\frac{3}{4}$ " diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an Aqueous Source of an Alkali Metal or Earth Alkali Metal Hydroxide to the Mixture.

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.

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.

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.

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.

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

(e) Forming a Reaction Medium Comprising a Non-Equilibrium Solution of Peracetic Acid.

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

16

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.

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).

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.

In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing Water.

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

(b) Introducing a Hydrogen Peroxide-Acetyl Precursor Solution to the Water.

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.

US 9,730,443 B2

17

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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

(c) Mixing the Hydrogen Peroxide-Acetyl Precursor Solution and the Water to Form a Mixture.

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

(d) Adding an Aqueous Source of an Alkali Metal or Earth Alkali Metal Hydroxide to the Mixture.

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.

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.

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.

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

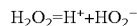
(e) Forming a Reaction Medium Comprising a Non-Equilibrium Solution of Peracetic Acid.

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.

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).

18

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:



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 perhydrolysis 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).

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%.

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.

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.

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.

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

Example 8

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

US 9,730,443 B2

19

reactants were introduced to the solution in one of three ways: simultaneously (referred to in Table VIII as “double”), sequentially (triacetin followed shortly by hydrogen peroxide), or by mixing the hydrogen peroxide and triacetin together and adding them in a single charge (referred to in Table VIII as “mixed”). All testing was performed at ambient temperature as the one-liter beaker was stirred with a magnetic stir bar. Using the ceric sulfate-iodometric titration method, the percent of PAA generated and the percent of hydrogen peroxide remaining were measured five minutes after introduction of the reactants to the buffer. The percent of the triacetin acetyl donor converted to PAA was calculated, assuming all three acetyl groups were available for perhydrolysis.

TABLE VIII

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 Remaining	% 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%

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

Example 9

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 peroxi-

20

de: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 a.

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

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

US 9,730,443 B2

21

at five minutes, corresponding to a yield of 62.9% assuming all three acetyl groups of triacetin were available for perhydrolysis.

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.

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

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.

Example 10

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.

22

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

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.

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

TABLE XII

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

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

Example 11

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.

US 9,730,443 B2

23

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

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.

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.

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

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

Example 12

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.

In the second test, the first test was repeated, except that the water was chilled soft water.

In the third test, the first test was repeated using three times the original amount of hydrogen peroxide: triacetin

24

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.

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.

Table XV summarizes the results obtained for the four tests and shows the initial and final solution temperatures, the pH of the solution after the addition of the 50% NaOH, the maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

TABLE XV

Test #	Initial Temp. (° F.)	Final Temp. (° F.)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

TABLE XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

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

US 9,730,443 B2

25

6.3% PAA. The data in Table XV indicate that the time of maximum conversion of triacetin was between one and four minutes. Thereafter, the amount of PAA in solution is reduced because it undergoes high pH degradation slowly over the following 10 minutes.

Example 13

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.

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.

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.

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.

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.

The rate of the reaction between the hydrogen peroxide and the triacetin to form PAA is dependent upon the tem-

26

perature 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.

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**.

Point-of-use **195** may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products; fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

Example 14

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.

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**.

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.

US 9,730,443 B2

27

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

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing flow rate of NaOH. For this mole ratio of hydrogen peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

Example 15

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.

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.

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.

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, Calif.). 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.

28

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.

All 3M *E. coli* Petrifilms and 3M Enterobacteriaceae Petrifilms were incubated at 35° C. for 24 hours. After incubation, the plates were enumerated.

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 log₁₀ 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.

The *E. coli* test solution treated with 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 6.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log₁₀ 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 log₁₀ 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.

TABLE XVIII

<i>E. coli</i> 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

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 log₁₀ 7.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.

The *Salmonella* solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 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 log₁₀ 6.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log₁₀ 4.95 CFU/mL remained (99.24% reduction).

TABLE XIX

<i>Salmonella typhimurium</i>			
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

US 9,730,443 B2

29

TABLE XIX-continued

<i>Salmonella typhimurium</i>			
Description	log ₁₀ CFU/ml remaining	log ₁₀ reduction	% reduction
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

The data in tables XVIII and XIX demonstrate that the 1% PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%, about equal to that of the Perasan MP-2, which was >99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

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.

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.

The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispersency, and lower surface tension.

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.

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.

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.

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.

30

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 surfactant, 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 homogenous mixture. The mixture is a freely-flowable solid which is readily discharged from the blender.

Example 16

A series of tests were performed to determine whether triacetin, a liquid at room temperature, could be blended with a solid source of hydrogen peroxide to form a solid bleaching and stain removal composition that did not clump or turn into a sticky, non-flowable mass. The components listed in Table XX were mixed together to form a solid peroxygen bleach precursor.

TABLE XX

Component	%
Sodium carbonate, anhydrous	26.3
Sodium percarbonate	58.9
Sodium sulfate decahydrate	13.8
Surfactant (60% sodium dodecylbenzene sulfonate)	1.0
Total	100

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 9.1 g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

TABLE XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely-flowable solid	None
2	Freely-flowable solid	None
3	Freely-flowable solid	None
4	Freely-flowable solid	None
5	Freely-flowable solid	None
6	Freely-flowable solid	None
7	Freely-flowable solid	None
8	Freely-flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45 g 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.

The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.

US 9,730,443 B2

31

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

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.

These surprising results are in contrast to the current belief that a liquid acetyl precursor, such as triacetin, could not be utilized with a solid source of hydrogen peroxide in a non-chlorine peroxygen bleaching and stain removal composition, for at least two reasons. First, when a non-chlorine peroxygen bleaching composition is used in residential and commercial laundering applications, the product must be a freely-flowable solid. Typically, the acetyl precursor in a non-chlorinated peroxygen bleach is present in amounts up to 10%. It was believed that blending a liquid at this level with the other dry components of the laundry bleach would create a sticky, clumping mass, rather than a freely-flowable solid, and would therefore not be acceptable to the user. Second, it was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

Example 17

Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.

TABLE XXIII

	%	Charge Weights, g
Components of Composition A		
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		
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

32

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.

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.

Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

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.

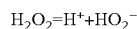
Neither composition exhibited significant exothermic behavior. However, composition A was hotter at the end of preparation and cooled more slowly than composition B. The temperature of composition A was 85° F. immediately after preparation, rose to 88° F. over the next ten minutes, and then fell slowly 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.

The solid peroxygen bleaching and stain removal composition described above may be used as follows.

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 5 g 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.

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.

While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:



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.

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.

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

US 9,730,443 B2

33

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.

Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

Example 18

Laundry swatches were made by cutting a tea towel into 50 equal 5x4 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.

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.

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. Pat. No. 7,651,724. At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75° F., the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104° F. had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H₂O₂). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75° F. at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104° F. at a pH of 11.2.

TABLE XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

TABLE XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426

34

TABLE XXV-continued

Time (min)	ppm PAA	ppm Hydrogen Peroxide
5.5	133	1494
7.8	122	1427
10.3	119	1405

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.).

A control swatch was obtained by taking one swatch at a time from each stain group and washing in city water at an elevated temperature (120° F.) for 10 minutes in the same manner as the treated swatches. After the wash, the swatches were immediately removed, wrung out by hand, and laid to dry.

TABLE XXVI

Type of Swatches	Description
Treated Swatches	Swatches subjected to bleaching for 10 minutes using bleaching formulation with triacetin and a 2-minute rinse with hard water
Control Swatches	Swatches subjected to only an elevated temperature (120° F.) hard water wash for 10 minutes
Non-Stained Swatches	Non-altered swatches

The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

TABLE XXVII

Type of Stain	Bleaching Formula at 64° F.	Bleaching Formula at 120° F.
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

US 9,730,443 B2

35

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 5 on grass stains or the chlorophyll pigment that was acetone-extracted from green grass.

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 10 invention that fall within the scope of the claims.

We claim:

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

- a. peracetic acid; 15
- b. hydrogen peroxide;
- c. triacetin;
- d. 1,2,3-propanetriol;
- e. an aqueous source of an alkali metal or earth alkali metal hydroxide; and 20
- f. water.

2. The solution of claim 1, wherein said solution has a pH of about 11.2 to about 13.37.

3. The solution of claim 1, wherein said peracetic acid is about 1% to about 7.1%. 25

* * * * *

36

EXHIBIT D



US009737072B2

(12) **United States Patent**
Harvey et al.

(10) **Patent No.:** **US 9,737,072 B2**

(45) **Date of Patent:** ***Aug. 22, 2017**

(54) **METHODS AND COMPOSITIONS FOR THE GENERATION OF PERACETIC ACID ON SITE AT THE POINT-OF-USE**

A01N 59/00 (2006.01)

C11D 3/395 (2006.01)

A01N 37/12 (2006.01)

B01J 19/24 (2006.01)

D06L 4/15 (2017.01)

(71) Applicant: **Enviro Tech Chemical Services, Inc.**,
Modesto, CA (US)

(72) Inventors: **Michael S. Harvey**, Modesto, CA (US);
Jonathan N. Howarth, Modesto, CA (US)

(73) Assignee: **Enviro Tech Chemical Services, Inc.**,
Modesto, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/063,293**

(22) Filed: **Mar. 7, 2016**

(65) **Prior Publication Data**

US 2016/0183531 A1 Jun. 30, 2016

Related U.S. Application Data

(62) Division of application No. 14/019,296, filed on Sep. 5, 2013, now Pat. No. 9,370,180, which is a division of application No. 13/065,553, filed on Mar. 24, 2011, now Pat. No. 8,546,449.

(51) **Int. Cl.**

A61K 31/19 (2006.01)

A01N 37/16 (2006.01)

C11D 3/39 (2006.01)

C11D 11/00 (2006.01)

(52) **U.S. Cl.**

CPC *A01N 37/16* (2013.01); *A01N 37/12*

(2013.01); *A01N 59/00* (2013.01); *B01J 19/24*

(2013.01); *C11D 3/3947* (2013.01); *C11D*

3/3955 (2013.01); *C11D 3/3956* (2013.01);

C11D 11/0041 (2013.01); *D06L 4/15*

(2017.01); *B01J 2219/24* (2013.01)

(58) **Field of Classification Search**

USPC 514/557

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2016/0183523 A1* 6/2016 Harvey C11D 3/3947
514/557

* cited by examiner

Primary Examiner — Rei-Tsang Shiao

(74) *Attorney, Agent, or Firm* — Audrey A. Millemann;
Weintraub Tobin

(57) **ABSTRACT**

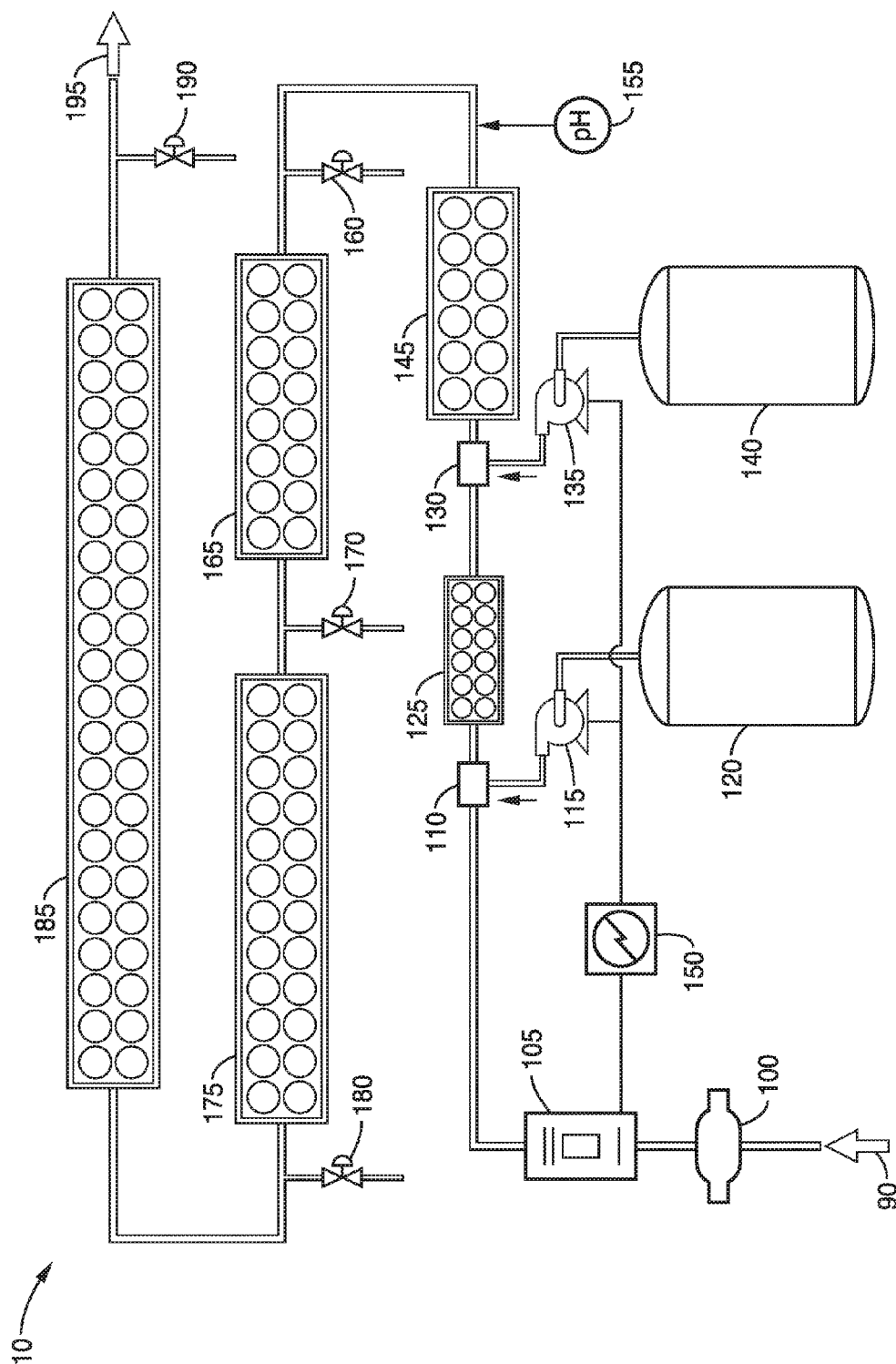
Methods for the generation of non-equilibrium solutions of peroxyacetic acid are disclosed. These methods comprise introducing triacetin and aqueous hydrogen peroxide to water, mixing, and then adding an aqueous source of an alkali metal or earth alkali metal hydroxide. Triacetin is converted rapidly and with a high conversion rate into peracetic acid. These methods produce solutions with a high level of peracetic acid.

3 Claims, 1 Drawing Sheet

U.S. Patent

Aug. 22, 2017

US 9,737,072 B2



US 9,737,072 B2

1

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

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a divisional application of co-pending U.S. patent application Ser. No. 14/019,296 filed on Sep. 5, 2013, which is a divisional of prior application Ser. No. 13/065,553 filed on Mar. 24, 2011, now U.S. Pat. No. 8,546,449 issued on Oct. 1, 2013, pursuant to 35 U.S.C. §§120 and 121, and hereby incorporates both applications by reference in their entirety.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

A. Liquid PAA Disinfectants and Sanitizers

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.

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

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

2

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.

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. Pat. 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.

Other attempts to make non-equilibrium solutions of PAA at the point-of-use are based on electrolytic processes. U.S. Pat. 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.

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, where-

US 9,737,072 B2

3

upon 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.

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).

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. Pat. 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.

4

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. Pat. 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.

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 side-stream 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.

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 tetraacetylenediamine (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.

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

B. Solid PAA Bleaches and Stain Removers

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, tetraacetylenediamine (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-

US 9,737,072 B2

5

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

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.

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

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.

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 hydro-

6

gen 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.

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%.

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.

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 limita-

US 9,737,072 B2

7

tions 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.

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.

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.

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.

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

FIG. 1 is a schematic representation of an example of a system that may be used to continuously or intermittently generate PAA for on a site having a point-of-use of peracetic acid. In another embodiment, a freely-flowable, solid peroxygen composition for use in laundry bleaching and stain removal is provided according to an embodiment.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

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

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

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

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

2. Experimental Methods

PAA and hydrogen peroxide in solution were determined using the ceric sulfate-sodium thiosulfate method. The method involves adding a known weight of sample contain-

8

ing 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:

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

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

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.

In circumstances where low concentrations of PAA were used, the modified DPD method (U.S. Pat. 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 ($76/71=1.07$).

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 ($34/71=0.479$).

US 9,737,072 B2

9

3. Liquid Compositions for Generating Non-Equilibrium Solutions of PAA on a Site Having a Point-of-Use

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.

The hydrogen peroxide-acetyl precursor solutions are prepared by the following steps.

(a) Introducing a Liquid Acetyl Precursor that is Soluble in Aqueous Hydrogen Peroxide to a Solution of Aqueous Hydrogen Peroxide.

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).

The mole ratio of hydrogen peroxide:triacetin is about 2.98:1 to about 12.84:1.

(b) Allowing the Acetyl Precursor and the Aqueous Hydrogen Peroxide to Mix to Form a Hydrogen Peroxide-Acetyl Precursor Solution.

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.

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.

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.

The hydrogen peroxide-acetyl precursor solutions prepared by this method may be used to generate non-equilibrium solutions of PAA on a site having a point-of-use of peracetic acid, in the methods described in section 4 below. The hydrogen peroxide-acetyl precursor solutions may be transported in any container suitable for transporting liquids, such as plastic tote bins of 275-330 gallons, drums of 15-55 gallons, five-gallon pails, one-gallon jugs, or other containers.

EXAMPLE 1

Triacetin (83.05 g) was added to 50% hydrogen peroxide solution (75 g) to form 158.05 g of a mixture. There was no

10

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.

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.

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.

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

Table I shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an increase in PAA. By the end of the 134-day study, the composition had lost 5.22% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone towards the generation of PAA, 11.67% PAA would have been generated. Because 6.87% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 2.15%. This loss of hydrogen peroxide was surprisingly small given that hydrogen peroxide is often used to destroy organic compounds by oxidation and the composition originally contained 52.55% of triacetin, an organic compound.

EXAMPLE 2

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.

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

US 9,737,072 B2

11

TABLE II-continued

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
173	18.49	4.43
201	15.67	3.51

Table II indicates that after 96 days, the generation of PAA maximized at 8.36% and corresponded to a loss of 10.94% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 24.45% PAA would have been generated. Because only 8.36% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 7.2%.

EXAMPLE 3

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 5.8:1 was prepared by adding triacetin (37.5008 g) to 50% hydrogen peroxide (65.2504 g) so that the mixture was 31.75% hydrogen peroxide and 36.5% triacetin, with the balance being water. The pH of the solution was 1.57 and the pH of a 1:100 dilution was 5.17. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table III shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of six days.

TABLE III

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	31.72	0.33
6	31.63	0.716

In this study, after six days, the mixture had lost only 0.09% hydrogen peroxide, yet had generated an additional 0.386% PAA. Had all the loss of hydrogen peroxide been due to the formation of PAA, only an additional 0.201% would have been generated. It is clear that the analytical methods employed for solutions that are high in hydrogen peroxide but low in PAA are subject to detection limit errors.

EXAMPLE 4

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 3.2:1 was prepared by adding triacetin (35.0 g) to 50% hydrogen peroxide (35.0 g) so that the mixture was 25% hydrogen peroxide and 50% triacetin, with the balance being water. The pH of the solution was 1.66 and the pH of a 1:100 dilution was 4.09. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table IV shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 22 days.

TABLE IV

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	25	0.62
8	24.51	1
15	24.17	1.17
22	23.68	1.14

12

Table IV indicates that after 15 days, the generation of PAA maximized at 1.17% and corresponded to a loss of 0.83% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 1.86% PAA would have been generated. Because only 1.17% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.31%.

EXAMPLE 5

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 4.8:1 was prepared by adding triacetin (37.50 g) to 50% hydrogen peroxide (56.25 g) so that the mixture was 30% hydrogen peroxide and 40% triacetin, with the balance being water. The pH of the solution was 1.67 and the pH of a 1:100 dilution was 4.62. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table V shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 43 days.

TABLE V

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	30.08	0.38
8	29.85	0.784
15	29.63	1.22
22	29.37	1.71
29	28.76	2.26
36	28.67	2.78
43	28.31	3.41

Table V shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by the associative increase of PAA. At the end of the 43-day study, the composition had lost 1.77% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 3.96% PAA would have been generated. Because only 3.41% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.24%.

EXAMPLE 6

A formulation containing hydrogen peroxide and triacetin in a mole ratio of 6.42:1 was prepared by adding triacetin (25.0007 g) to 50% hydrogen peroxide (50.0007 g) so that the mixture was 33.33% hydrogen peroxide and 33.33% triacetin, with the balance being water. The pH of the solution was 1.56 and the pH of a 1:100 dilution was 5.15. To accelerate degradation, the sample was placed in an incubator set for 86-87° F. Table VI shows the percent of hydrogen peroxide remaining and the percent of PAA generated over a period of 36 days.

TABLE VI

Days of Study	% Hydrogen Peroxide Remaining	% PAA Generated
1	33.13	0.81
8	32.88	1.35
15	32.61	1.88
22	31.69	2.58
29	31.75	3.03
36	31.29	3.28

Table VI shows that although there was a steady depletion in hydrogen peroxide, it was accompanied by an associative

US 9,737,072 B2

13

increase of PAA. At the end of the 36-day study, the composition had lost 1.84% hydrogen peroxide. Had all of the depleted hydrogen peroxide gone toward the generation of PAA, 4.11% PAA would have been generated. Because only 3.28% PAA was generated, unaccounted losses of hydrogen peroxide amounted to 0.37%.

EXAMPLE 7

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.

After 295 days of storage, the mixture was analyzed for total peroxygen recovered (expressed as hydrogen peroxide) to determine the percent loss of peroxygen. Using the ceric sulfate-iodometric titration method, the PAA generated and the hydrogen peroxide remaining were measured. The total peroxygen recovered after 295 days and the theoretical initial concentrations are shown in Table VII. All peroxygen is expressed as % hydrogen peroxide.

TABLE VII

	Initial Theoretical %	% (after 295 days)
Hydrogen Peroxide Recovered	27.17	15.20
PAA formed	0	15.57
Hydrogen Peroxide Reacted to form PAA	0	6.97
Total Recovered Hydrogen Peroxide	27.17	22.17
Total Hydrogen Peroxide Unproductive Loss		5.00

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

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.

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

(a) Providing Water.

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

14

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.

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

(b) Introducing a Hydrogen Peroxide-Acetyl Precursor Solution to the Water.

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.

A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

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.

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 a hydrogen peroxide-acetyl precursor solution, then in step (c) the liquid acetyl precursor and the aqueous hydrogen peroxide are mixed with the water to form a mixture.

(c) Mixing the Hydrogen Peroxide-Acetyl Precursor Solution and the Water to Form a Mixture.

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

US 9,737,072 B2

15

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 $\frac{3}{4}$ " pipe, a static mixer of $\frac{3}{4}$ " diameter and 6" long, and a velocity of about 1 gal/min., mixing should be accomplished in less than about one second.

(d) Adding an Aqueous Source of an Alkali Metal or Earth Alkali Metal Hydroxide to the Mixture.

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.

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.

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.

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.

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

(e) Forming a Reaction Medium Comprising a Non-Equilibrium Solution of Peracetic Acid.

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.

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).

This method may also include an optional step after step (e) of sampling the reaction medium at various times after

16

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.

5 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. 10 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.

30 In another embodiment, a method of continuously or intermittently generating a non-equilibrium solution of PAA on a site having a the point-of-use in a batch process comprises the following steps:

(a) Providing Water.

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

(b) Introducing a Hydrogen Peroxide-Acetyl Precursor Solution to the Water.

45 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.

55 A preferable liquid acetyl precursor is triacetin. When triacetin is used, a hydrogen peroxide-triacetin solution is introduced.

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.

60 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.

65 As an alternative to step (b), the liquid acetyl precursor and the solution of aqueous hydrogen peroxide may be

US 9,737,072 B2

17

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

(c) Mixing the Hydrogen Peroxide-Acetyl Precursor Solution and the Water to Form a Mixture.

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

(d) Adding an Aqueous Source of an Alkali Metal or Earth Alkali Metal Hydroxide to the Mixture.

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.

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.

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.

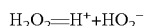
Step (d) may be performed after step (c), or it may be performed simultaneously with step (b).

(e) Forming a Reaction Medium Comprising a Non-Equilibrium Solution of Peracetic Acid.

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.

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).

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:



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 perhydrolysis reaction of the acetyl precursor. When the acetyl precursor is triacetin and all three

18

acetyl groups are reacted, then the product of the perhydrolysis reaction is 1, 2, 3-propanetriol (glycerine).

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%.

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.

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.

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.

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

EXAMPLE 8

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.

US 9,737,072 B2

19

20

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 Remaining	% 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%

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

EXAMPLE 9

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 a.

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

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.

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.

US 9,737,072 B2

21

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

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with the increasing mole ratio of NaOH:TA. For all four mole ratios employed, the maximum amount of PAA was generated between three and six minutes. The optimum mole ratio of NaOH:TA was 6:1 as it resulted in an efficient utilization of triacetin converted into PAA, and because the pH of the resulting reaction medium would have less impact on the pH of the receiving water than the higher pH of the reaction medium resulting from the 8:1 mole ratio.

EXAMPLE 10

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

TABLE XI

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

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 conver-

22

sion of triacetin into PAA of 63.8%, assuming that all three acetyl groups of triacetin were available for perhydrolysis.

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

TABLE XII

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

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

EXAMPLE 11

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

TABLE XIII

Time (min)	% PAA Generated	% Hydrogen Peroxide Remaining	% Triacetin Converted to PAA (3 acetyls)
1	0.247	0.207	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

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.

US 9,737,072 B2

23

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.

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

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

EXAMPLE 12

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.

In the second test, the first test was repeated, except that the water was chilled soft water.

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.

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

24

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.

Table XV summarizes the results obtained for the four tests and shows the initial and final solution temperatures, the pH of the solution after the addition of the 50% NaOH, the maximum percent of PAA generated, the time of maximum PAA generation, and the percent of hydrogen peroxide remaining.

TABLE XV

Test #	Initial Temp. (° F.)	Final Temp. (° F.)	Final pH	Max. % PAA Generated (time, min)	% Hydrogen Peroxide Remaining
1	NM	NM	12.14	1.71 (1)	0.58
2	38	50	12.67	2.1 (4)	0.43
3	44	88	12.77	6.3 (1)	1.18
4	34	92	13.17	7.2 (1)	1.88

NM = not measured

Table XVI shows the percent of hydrogen peroxide converted overall, the percent of hydrogen peroxide converted to PAA, and the percent of triacetin converted to PAA (assuming that all three acetyl groups on triacetin are available for conversion to PAA) for each of the tests in Table XV.

TABLE XVI

Test #	% Hydrogen Peroxide Converted Overall	% Hydrogen Peroxide Converted to PAA (at maximum conversion time)	% Triacetin Converted to PAA (3 acetyls)
1	67.8	88.1	69.7
2	68.8	94.4	85.8
3	71.6	94.3	85.7
4	66.1	88.1	73.8

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.

EXAMPLE 13

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.

US 9,737,072 B2

25

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.

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.

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.

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.

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

26

minutes, and sampling port **190** in five minutes, to permit sampling at different time intervals.

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**.

Point-of-use **195** may be recirculating cooling water; municipal wastewater; poultry chill tank water; water used to sanitize meat, poultry, or seafood products; fruit and vegetable rinse water; or water used to clean and sanitize equipment used in the dairy, food, or beverage processing industries.

EXAMPLE 14

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.

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**.

The percent of PAA generated was measured by quenching samples drawn through the sampling ports in mineral acid, followed by use of the ceric sulfate-iodometric titration method. Table XVII summarizes the results of several trials where it was sought to maximize the conversion of triacetin into PAA and minimize the amount of 50% NaOH used.

TABLE XVII

Trial #	Sample Port	% PAA Generated	% Triacetin Converted to PAA	Hydrogen Peroxide-Triacetin Mix Flow Rate (mL/min)	NaOH Flow Rate (mL/min)	pH (PAA solution)
1	160	1.083	65.42	115.73	112.11	~13
2	170	1.073	64.82	115.73	112.11	13.19
3	160	0.955	57.32	116.79	122.12	13.37
4	160	1.058	63.39	116.79	114.93	13.11
5	160	1.061	63.3	116.79	98.1	12.9
6	160	1.102	68.96	110.82	85.01	12.91
7	170	1.055	55.59	132.64	99.77	12.95
8	160	0.978	59.91	115.5	74	12.62
9	180	0.936	56.7	114.25	78	12.64

It can be seen that the amount of PAA generated, and hence the conversion of triacetin into PAA, increased with

US 9,737,072 B2

27

the increasing flow rate of NaOH. For this mole ratio of hydrogen peroxide:triacetin of 3.8:1, the maximum amount of PAA was generated between 30 seconds (sample port 160) and two minutes (sample port 180) from the time the NaOH was added at injection quill 130. The flow rate of 74-78 mL/min of 50% NaOH was the optimum flow rate as it resulted in an efficient utilization of triacetin converted into PAA, consumed only a moderate amount of 50% NaOH, and had a lower pH that would have less impact on the pH of the receiving water.

EXAMPLE 15

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.

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.

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.

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, Calif.). 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.

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.

All 3M *E. coli* Petrifilms and 3M Enterobacteriaceae Petrifilms were incubated at 35° C. for 24 hours. After incubation, the plates were enumerated.

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.*

28

coli test solution started with log₁₀ 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.

The *E. coli* test solution treated with 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 6.74 CFU/mL after one minute. This corresponds to 43.48% reduction. After five minutes, log₁₀ 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 log₁₀ 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.

TABLE XVIII

<i>E. coli</i> 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

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 log₁₀ 7.07 CFU/mL prior to being treated with PAA from Perasan MP-2 or with the 1% PAA solution.

The *Salmonella* solution treated with a nominal 1.0 ppm PAA from Perasan MP-2 contained a log₁₀ 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 log₁₀ 6.69 CFU/mL after one minute. This corresponds to 58.31% reduction. After five minutes, log₁₀ 4.95 CFU/mL remained (99.24% reduction).

TABLE XIX

<i>Salmonella typhimurium</i>			
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

The data in tables XVIII and XIX demonstrate that the 1% PAA had antimicrobial efficacy. After five minutes, the efficacy of this PAA was 99.24%, about equal to that of the Perasan MP-2, which was >99.9999%. The difference in efficacy at one minute was likely not of statistical significance, given that the comparison was only at the one-minute interval.

5. Solid Compositions for Bleaching and Stain Removal

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,

US 9,737,072 B2

29

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.

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.

The composition may optionally contain other components to improve performance. These components may prevent soil redeposition, sequester water hardness, increase dispersency, and lower surface tension.

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.

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.

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.

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.

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 surfactant, 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 homogenous mixture. The mixture is a freely-flowable solid which is readily discharged from the blender.

EXAMPLE 16

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.

30

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

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 9.1 g of liquid triacetin was blended into 100 g of the solid peroxygen bleach precursor set forth above.

TABLE XXI

Wt. of triacetin added to solid peroxygen bleach precursor (g)	Freely-flowable solid or sticky and clumping	Odor of PAA
1	Freely-flowable solid	None
2	Freely-flowable solid	None
3	Freely-flowable solid	None
4	Freely-flowable solid	None
5	Freely-flowable solid	None
6	Freely-flowable solid	None
7	Freely-flowable solid	None
8	Freely-flowable solid	None
8.45	Freely-flowable solid	None
9	Sticky and clumping	None
9.1	Sticky and clumping	None

Surprisingly, even though triacetin is a liquid, the solid peroxygen bleach precursor (100 g) could be blended with up to 8.45 g 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.

The solid peroxygen bleaching and stain removal composition was calculated to contain the following percentage of components, listed in Table XXII.

TABLE XXII

Component	%
Sodium carbonate, anhydrous	24.14
Sodium percarbonate	53.90
Sodium sulfate decahydrate	12.56
Surfactant (90% sodium dodecylbenzene sulfonate)	0.95
Triacetin	8.45
Total	100

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.

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

US 9,737,072 B2

31

with the other dry components of the laundry bleach would create a sticky, clumping mass, rather than a freely-flowable solid, and would therefore not be acceptable to the user. Second, it was assumed that a liquid acetyl precursor would interact with the solid source of hydrogen peroxide and any free water or water of crystallization associated with other components, and thus form PAA in the product during storage, before being introduced to the aqueous bleaching medium. The high volatility and strong odor of the PAA would be unacceptable to the user of such a product.

EXAMPLE 17

Two solid peroxygen bleaching and stain removal compositions were prepared with the components listed in Table XXIII.

TABLE XXIII

	%	Charge Weights, g
Components of Composition A		
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		
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

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.

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.

Premix 2 was blended in portions into Premix 1, and the final solid composition was mixed well by hand.

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.

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 composi-

32

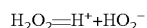
tion B was 80° F. immediately after preparation, rose to 81° F. over the next twenty minutes, and then fell slowly to 65° F.

The solid peroxygen bleaching and stain removal composition described above may be used as follows.

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 5 g 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.

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.

While not wishing to be bound by theory, it is believed that under elevated pH conditions, hydrogen peroxide dissociates according to the following equation:



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.

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.

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.

Fifth, the article is allowed to dry. Any suitable means of drying the bleached articles may be employed. This includes the use of centrifugal forces to mechanically dewater the articles prior to introducing the wet articles to another machine before the articles are tumbled in a stream of hot air. Alternatively, the articles may be allowed to air dry without the use of externally-applied heat.

EXAMPLE 18

Laundry swatches were made by cutting a tea towel into 50 equal 5x4 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

US 9,737,072 B2

33

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.

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.

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. Pat. No. 7,651,724. At each temperature, the composition (1.0 g) was weighed out into a glass beaker (100 mL). To the beaker, city water (99 mL) was added while mixing on a stir plate. The pH and PAA generation profile was then monitored over the next 10-13 minutes to model the times of a typical low temperature and high temperature bleaching cycle. For city water at 75° F., the initial pH measured 11.2 and the PAA measured highest at 10.5 minutes (123 ppm PAA and 1594 ppm hydrogen peroxide). The test with city water at 104° F. had the same initial pH of 11.2, but the PAA measured highest at 5.5 minutes (133 ppm PAA and 1494 ppm H₂O₂). Table XXIV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 75° F. at a pH of 11.2. Table XXV shows the amount of PAA generated and the amount of hydrogen peroxide remaining over time at 104° F. at a pH of 11.2.

TABLE XXIV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
1	61	1717
3	106	1673
5.2	113	1694
7.3	121	1571
10.5	123	1594
13.5	120	1547

TABLE XXV

Time (min)	ppm PAA	ppm Hydrogen Peroxide
0.5	72	1569
2.8	125	1426
5.5	133	1494
7.8	122	1427
10.3	119	1405

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.).

34

A control swatch was obtained by taking one swatch at a time from each stain group and washing in city water at an elevated temperature (120° F.) for 10 minutes in the same manner as the treated swatches. After the wash, the swatches were immediately removed, wrung out by hand, and laid to dry.

TABLE XXVI

Type of Swatches	Description
Treated Swatches	Swatches subjected to bleaching for 10 minutes using bleaching formulation with triacetin and a 2-minute rinse with hard water
Control Swatches	Swatches subjected to only an elevated temperature (120° F.) hard water wash for 10 minutes
Non-Stained Swatches	Non-altered swatches

The bleaching ability of the test swatches was obtained by visual comparison of the treated swatches to the control swatches (treated with water only) and the non-stained swatches. The scale of bleaching ability of the composition was rated on a scale of 0 to 10, with 0 representing no apparent bleaching or stain removal properties of the swatches compared to the control and 10 representing bleaching of swatches to the original color (i.e., identical to the non-stained swatches). Three individuals rated the bleaching ability of the triacetin-containing formulation on the swatches independently. The average ratings from the three individuals are shown in Table XXVII.

TABLE XXVII

Type of Stain	Bleaching Formula at 64° F.	Bleaching Formula at 120° F.
Black Tea	5	8
Black Coffee	2	8
Red Wine	3	7
Blood (pork)	3	3
Extracted chlorophyll	0	0
Grass Stains	0	1

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.

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.

We claim:

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

- aqueous hydrogen peroxide;
- triacetin;
- a trace amount of peracetic acid; and
- water.

2. The solution of claim 1, 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.

US 9,737,072 B2

35

3. The solution of claim 2, 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

36

EXHIBIT E



May 20, 2024

VIA EMAIL AND OVERNIGHT DELIVERY

Clean Chemistry
Attn: Nic Gardiner
2555 55th Street
Suite 104
Boulder, CO 80301

RE: Non-exclusive License of Enviro Tech Patents

Dear Nic,

We are following up on the phone call between you and Julie Gallucci on May 15, 2024, where Julie expressed Enviro Tech's position.

Enviro Tech is the patent owner of US Patent Nos 9,737,072; 9,370,180; 10,004,230; 8,546,449; and 9,363,997. These patents disclose the starting materials and process to produce peroxyacetic acid.

Clean Chemistry's Food Contact Notification (FCN) was approved on February 14, 2024, and recently became public. The FCN includes an Environmental Assessment which is a National Environmental Policy Act (NEPA) Submission. The Environmental Assessment describes Clean Chemistry's process for generating PeroxyMax in detail.

In light of the Environmental Assessment, we believe that you may wish to have your patent counsel examine the above listed patents to determine whether a non-exclusive license under the patent is needed. We would be willing to consider additional information provided by you, even under a non-disclosure agreement if necessary, to evaluate the propriety of a patent license. Please let us know your answer on or before **Monday June 3, 2024**.

Sincerely,

A handwritten signature in cursive script that reads "Kristin Rinaldi".

Kristin Rinaldi, *Senior Vice President, General Counsel and Secretary*

500 Winmoore Way* Modesto, CA 95358 * (209) 581-9576 * Fax (209) 581-9653

www.envirotech.com * www.stabilizedbromine.com

EXHIBIT F



Advanced Oxidation Technology for any Water Treatment Application

PeroxyMAX™ is Clean Chemistry's patented high-performing oxidation chemical technology that is a **safer, more effective and more economical alternative to traditional oxidant and biocides.**

Registered with the EPA as a biocide, PeroxyMAX is formulated to generate large quantities of reactive oxygen species (ROS) for a wide range of uses. Proven in industries as diverse as energy, pulp and paper and water cooling, PeroxyMAX applications include water treatment, microbial control, sulfide removal, well remediation, odor control, cleaning and sanitization, fermentation additive and pulp delignification, bleaching and brightening.

Key PeroxyMAX Features:

- **Low/reduced capital** and operating costs
- **Greater compatibility** with other water treatment chemicals
- **Less damaging** or corrosive to equipment
- **Less aggressive** towards sensitive metals, polymers and elastomers
- **Chemical residuals generally recognized as safe** (GRAS FDA designation)
- **Ability to target contaminants** over other materials
- **No odor or harmful fumes**
- **Safer mixing/manufacturing process:**
PeroxyMAX components are non-flammable, non-

explosive and can be stored on site prior to mixing.



The Chemistry Behind PeroxyMAX

PeroxyMAX is an activated alkyl peroxide formulation in water that efficiently generates reactive oxygen species (ROS) at a rate that is practical to dispense as a liquid product. The ROS “supercharges” the oxidative activity of the parent peroxide. The primary ROS in PeroxyMAX is singlet oxygen, which is molecular oxygen (O₂) in an excited state. The combination of oxidizing species in PeroxyMAX provides enhanced performance while generating a significant oxidation-reduction potential signature which can be monitored and correlated to concentration or efficacy in a treatment process.

Flexible Deployment Options

PeroxyMAX can be safely generated on-demand, near the point of application, and injected into the water stream where it is most needed: at the wellsite, at a pulp mill bleaching plant or on a food processing production line. In these applications, other oxidants are more challenging to use due to safety, odor, corrosion or chemical compatibility limitations.

	 HIGHLY CORROSIVE	 OXIDIZING HAZARD	 FLAMMABLE	 ENVIRONMENTAL HAZARD	 IRRITANT, ACUTE TOXICITY	 TOXIC
PEROXYMAX	—	—	—	—	—	—
Chlorine Dioxide	X	X	X	—	X	X
Peracetic Acid (PAA)	X	—	X	X	X	—
Chlorine Bleach	X	—	—	X	—	—

During actual application, PeroxyMAX provides lower risk compared to traditional water treatment options.
(Hazards showing empty cells in the table are not applicable to the listed chemical.) The icons pictured are not intended to align with the OSHA HazComm pictograms.



The Smart Chemical Treatment Platform

This small-footprint platform requires less power than a household dishwasher. A standard 3 ft by 4 ft sized system can produce 400 to 2000 pounds of PeroxyMAX a day. Systems can be scaled up or down to meet applications requirements and space constraints.

For mobile installations, our **PeroxyMAX Oxidation Technology Trailer** utilizes smart technology, enhanced automation, data driven quality control and adaptable chemical dosing for improved onsite operations. Quick setup, fast deployment and full cloud-backed connectivity allow PeroxyMAX technology to be quickly applied at any water treatment site.

ABOUT DEPLOYMENT

Read More About our PeroxyMAX Technology

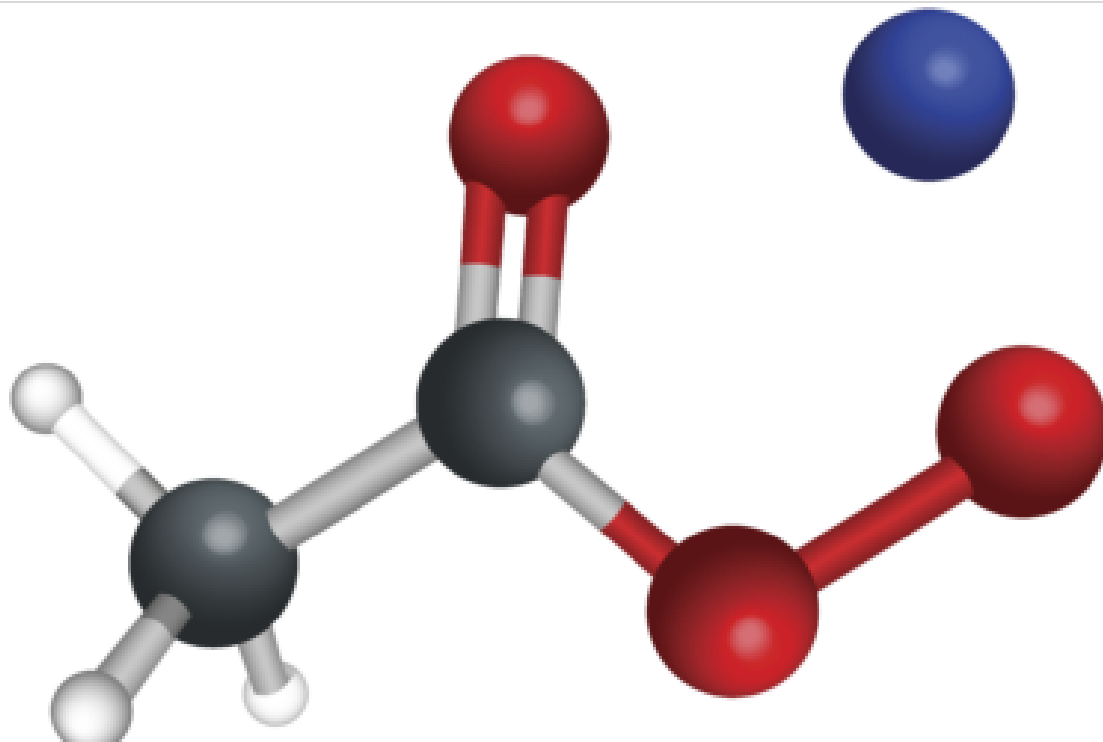
THE CLEAN CHEMISTRY BLOG



PeroxyMAX™ versus Peracetic Acid

by Clean Chemistry | Nov 10, 2023 | Blog

For years, peracetic acid (PAA) has been the go-to oxidizer for water treatment. However, safety and economic concerns have led some industries to look for alternatives. The American Industrial Hygiene Association (AIHA) The Synergist blog lists some of the risks...



Reactive Oxygen Species (ROS): The Secret Behind the Chemistry

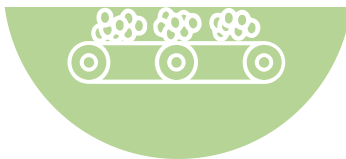
by Wayne Buschmann | Oct 6, 2023 | Blog

Many industries use water as a main component of their operations. With a growing trend toward reuse and recycling, operators from industries as diverse as food processing, paper mills and oil and gas sites are looking at the economics of water treatment. The industry...

[« Older Entries](#)

Discover Our Top Markets





Get Started with Clean Chemistry

"*" indicates required fields

*First Name

*Last Name

*Email Address

*Phone Number

*How can we help you?



SUBMIT



© 2012-2024 Clean Chemistry. All Rights Reserved.



P: (303) 440 – 8329

E: connect@cleanchemi.com

1900 S. Sunset Street, Suite 1E, Longmont, CO 80501

6107 S. County Rd 1273, Midland, TX 79706

EXHIBIT G

PART IV ENVIRONMENTAL INFORMATION

SECTION B - ENVIRONMENTAL ASSESSMENT

1. **Date:** February 1, 2024
2. **Notifier:** Clean Chemistry Inc.
3. **Address:** 2555 55th St.
Suite 104
Boulder, CO 80301

TSG Consulting (Agent)
1150 18th Street NW, Suite 475
Washington DC 20036

4. Description of Proposed Action

a. Requested Action

The action identified in this food contact notification (FCN) is to provide for the use of the food contact substance (FCS) identified as an aqueous mixture of peracetic acid (PAA), hydrogen peroxide (HP), sodium acetate, and glycerin (or glycerol), in the production and preparation of: whole or cut meat and poultry; processed and pre-formed poultry and meat; fruits and vegetables; fish and seafood; grains of wheat, corn and rice; shell and hardboiled peeled eggs, whey protein concentrate, lactose, brines, sauces, and marinades; and, aseptic filling and packaging systems.

When used as intended, the components of the FCS mixture will not exceed:

- 1) As an antimicrobial agent in spray, wash, rinse, dip, chill, and scald process water, ice, or brine used in the production, processing, and preparation of whole or cut meat carcasses, parts, trim, and organs at a maximum use level of 2000 ppm peracetic acid and 44.4 ppm hydrogen peroxide;
- 2) As an antimicrobial agent in spray, wash, rinse, dip, chill, and scald process water, ice, or brine used in the production, processing, and preparation of whole or cut poultry carcasses, parts, trim, and organs at a maximum use level of 2000 ppm peracetic acid and 44.4 ppm hydrogen peroxide;
- 3) As an antimicrobial agent in process water, ice, or brine used for washing, rinsing, or cooling of processed and preformed meat at a maximum use level of 495 ppm peracetic acid and 11 ppm hydrogen peroxide;

- 4) As an antimicrobial agent in process water, ice, or brine used for washing, rinsing, or cooling of processed and preformed poultry at a maximum use level of 495 ppm peracetic acid and 11 ppm hydrogen peroxide;
- 5) As an antimicrobial agent in process water or ice for washing, rinsing, chilling or processing fruits and vegetables in food processing facilities at a maximum use level of 600 ppm peracetic acid and 13.3 ppm hydrogen peroxide;
- 6) As an antimicrobial agent in process water and ice used to commercially prepare fish and seafood at a maximum use level of 230 ppm peracetic acid and 5.1 ppm hydrogen peroxide;
- 7) As an antimicrobial agent in applied during the tempering and before milling of grains of wheat, corn, and rice applied at a level not to exceed 3% by weight of the grain at a maximum use level of 6000 ppm peracetic acid and 133.3 ppm hydrogen peroxide;
- 8) As an antimicrobial agent in water for washing shell eggs at a maximum use level of 2000 ppm peracetic acid and 44.4 ppm hydrogen peroxide;
- 9) As an antimicrobial agent in spray, wash, dip, rinse, mist, or chiller water for hard boiled, peeled eggs at a maximum use level of 2000 ppm peracetic acid and 44.4 ppm hydrogen peroxide;
- 10) As an antimicrobial additive to liquid, pasteurized whey used in the production of whey protein concentrate at a maximum use level of 15 ppm peracetic acid and 0.33 ppm hydrogen peroxide;
- 11) As an antimicrobial to control microorganisms in wash water used to manufacture lactose at a maximum use level of 30 ppm peracetic acid and 0.67 ppm hydrogen peroxide;
- 12) As an antimicrobial agent used in brines, sauces, and marinades applied either on the surface or injected into processed or unprocessed, cooked, or uncooked, whole or cut poultry parts or pieces at a maximum use level of 50 ppm peracetic acid and 1.1 ppm hydrogen peroxide;
- 13) As an antimicrobial agent used in surface sauces and in marinades applied on processed and preformed meat and poultry products at a maximum use level of 50 ppm peracetic acid and 1.1 ppm hydrogen peroxide; and,
- 14) As an antimicrobial additive that may be used alone or in combination with other processes in the commercial sterilization of aseptic filling systems and glass and plastic food packaging and their enclosures prior to filling, except for use on food packaging used in contact with infant formula or human milk or on aseptic filling equipment used to fill such packaging, at 4500 ppm peracetic acid and 100 ppm hydrogen peroxide.

The FCS is not for use in contact with infant formula and human milk. The FCS is also not for use on food packaging used in contact with infant formula and human milk or on aseptic filling equipment used to fill such packaging. Such uses were not included as part of the intended use of the substance in the FCN.

b. Need for Action

The FCS reduces and/or eliminates pathogenic and non-pathogenic microorganisms that may be present on the food during production.

The purpose of this FCN is to propose uses for the FCS in order to address current and future needs of food processors and government agencies for improving food safety. Using the FCS provides more options for antimicrobial interventions, allowing the food industry to improve processing techniques and provide greater flexibility in terms of time, concentration, application method (e.g., spray vs. immersion) to improve the control of food pathogens.

c. Locations of Use/Disposal

The FCS is intended for use in meat and poultry, fruit and vegetable, fish and seafood, grain, egg, cheese, and lactose processing plants and filling and packaging facilities throughout the United States. It is expected that on-site wastewater treatment facilities will discharge to publically owned treatment works (POTW). During the onsite treatment process, very minor quantities of the solution are lost to evaporation. When used aboard fishing vessels, the water containing the FCS is expected to be disposed back into the open waters in compliance with local fishing discharge regulations.

1) Whole or Cut Meat and Poultry Processing

EPA requires meat and poultry processors to meet specific effluent pre-treatment standards.¹ Therefore, the waste process water containing the FCS is expected to be released to the processing plant's wastewater treatment facility before being discharged either to surface waters under National Pollution Discharge Elimination System (NPDES) permitting or to POTW.

In poultry processing facilities the diluted FCS is applied to poultry carcasses, organs, parts, or trim by an immersion dip or in a spray cabinet. Carcasses are carried on a conveyor through a spray cabinet and then submerged in the chiller baths. Parts and organs may also be chilled by submersion in baths containing the FCS. Chiller baths typically include a "main chiller" bath and a "finishing chiller" bath, which both contain the FCS. After the diluted FCS is sprayed onto the carcasses, or the carcasses are removed from an immersion dip, most of it drains off of the poultry. The waste solution runs into drains and enters the poultry processing plant water treatment facility. All water is collected and treated by the water treatment facility before being sent to a POTW. Very small quantities of this water would be lost to evaporation.

In meat processing facilities the diluted FCS is applied to meat carcasses or parts by spraying carcasses suspended on a moving conveyor line or rail system. The carcasses are carried into a spray cabinet where the dilute FCS solution is evenly applied onto the surface of the meat. The carcasses exit the spray cabinet and continue through the processing line. In some instances, meat parts are placed in a dip tank containing the diluted FCS in order to ensure full contact with the intervention treatment. After the diluted FCS is applied to the carcass, most of it drains off of the meat. This water ultimately runs into drains and enters the meat processing plant water treatment facility before being sent to a POTW. Very small quantities of water would be lost to evaporation.

¹ US EPA Meat and Poultry Products Effluent Guidelines, 40 CFR Part 432 <https://www.epa.gov/eg/meat-and-poultry-products-effluent-guidelines>.

2) Processed and Preformed Meat and Poultry

The FCS is used as a treatment for washing, rinsing, and cooling water applied to processed and pre-formed meat and poultry products. Most of the solution drains off the product.

3) Fruit and Vegetable Processing Facilities

Produce may be washed by submersion, spray, or both.² The FCS components that would enter environment will result from its use in the fruit and vegetable processing water and the subsequent disposal of such water draining into the processing plant wastewater treatment facility. There may also be direct discharge to surface waters from use of the PAA product in fruit and vegetable processing facilities.

4) Fish and Seafood Processing Facilities

Land Based Seafood Processing Facilities: Seafood products are caught in open waters or grown in seafood farms. Caught seafood products are sorted and separated into parts. Parts of seafood products are then flash frozen and packaged. The diluted FCS is sprayed directly onto the raw or processed seafood products before flash-freezing. The bulk of the solution drains off of the seafood products. The waste solution ultimately runs into drains and enters the seafood processing plant water treatment facility. All of this water is collected and treated by the facility prior to it being sent to a POTW or discharged directly to surface water in accordance with the plants' NPDES permit. Direct discharge to surface water is considered the worst-case scenario as it does not take into account any further treatment that may occur at a POTW. Very small quantities would be lost to evaporation into the air.

The diluted FCS may also be frozen into ice and then packaged with the frozen seafood product. The dilute frozen product will eventually thaw and drain off the seafood products at downstream facilities in the supply chain (e.g. grocery stores). This waste solution ultimately runs into drains and is sent to a POTW.

On-Board Seafood Processing: The proposed use in seafood and fish processing also includes use aboard fishing vessels during the initial evisceration and cleaning of freshly caught seafood. It is expected that wastewater will be discharged into the ocean where the peroxygen components in the FCS would have a very short half-life. In this discharge case, the component dilution residuals into the ocean would be impossible to calculate, and the resultant concentration of the components in the ocean would be negligible. Direct discharge of wastewater is an accepted practice within the fishing industry.

5) Grain Milling

The FCS is proposed for use as an antimicrobial agent for process water applied during the tempering and before milling of grains of wheat, corn, and rice. The primary pathway for the FCS to reach the environment is by the use and disposal of the FCS.

² U.S. Food and Drug Administration (February 2008) *Guidance for Industry: Guide to Minimize Microbial Food Safety Hazards of Fresh-cut Fruits and Vegetables*, Section VIII.C.2.b, <https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-guide-minimize-microbial-food-safety-hazards-fresh-cut-fruits-and-vegetables>

Following appropriate use, waste process water containing the diluted FCS solution will be disposed of at industrial wastewater treatment facilities established at processing plant use sites, in combination with publicly owned treatment works (POTWs), or privately owned treatment plants. For processing plants with active National Pollutant Discharge Elimination System (NPDES) permits (i.e., direct dischargers), FCS-containing wastewater will be treated on-site before discharge to surface waters or reuse. For processing plants without NPDES permits (i.e., indirect dischargers), wastewater that contains diluted FCS material is collected and treated by the facility. Wastewater treated at processing facilities is then directed through sanitary sewer systems into POTWs for standard wastewater treatment before movement into aquatic environments (i.e., surface water).

6) Egg Processing Facilities

The FCS is intended for use as an antimicrobial agent in processing water or ice used for washing, rinsing, storing, cooling and otherwise processing of peeled, hard-boiled eggs and shell eggs in food processing facilities throughout the United States.

Following appropriate use, waste process water containing the diluted FCS solution will be disposed of at industrial wastewater treatment facilities established at processing plant use sites, in combination with publicly owned treatment works (POTWs), or privately owned treatment plants. For processing plants with active National Pollutant Discharge Elimination System (NPDES) permits (i.e., direct dischargers), FCS-containing wastewater will be treated on-site before discharge to surface waters or reuse. For processing plants without NPDES permits (i.e., indirect dischargers), wastewater that contains diluted FCS material is collected and treated by the facility. Wastewater treated at processing facilities is then directed through sanitary sewer systems into POTWs for standard wastewater treatment before movement into aquatic environments (i.e., surface water).

7) Whey Pasteurization Facilities

The FCS is added directly to ingredient mixtures of frozen dessert mixes and ready-to-drink beverages containing whey protein, prior to pasteurization, in processing facilities throughout the United States. No environmental introductions are anticipated at the locations of use. The only environmental introductions will be due to residential disposal of human waste products. Wastewater containing the FCS will be diluted and treated at a Publicly Owned Treatment Works (POTW) prior to being combined with surface waters.

8) Lactose Production Facilities

FCS is used at the end of the lactose production by injecting FCS using flow-proportional dispensing equipment in the final stage "refining process", just prior to the TEMA separator (which is the stage that separates the liquid from the crystal lactose just prior to drying).

During the subsequent dehydration process the lactose, and a small amount of the FCS that remains, is subjected to drying temperatures of 195-210°F. Peroxy compounds cannot exist in a dehydrated form, and thus decompose to their degradation products carbon dioxide, oxygen and water. Small amounts of the degradation byproducts may remain as a result of the dehydration process.

The FCS substance, if accidentally discharged or released as over-flow from the process area, would be directed to the food plant wastewater discharge system, industrial wastewater treatment facilities established at processing plant use sites, in combination with publicly owned treatment works (POTWs), or privately owned treatment plants. For processing plants with active National Pollutant Discharge Elimination System (NPDES) permits (i.e., direct dischargers), FCS-containing wastewater will be treated on-site before discharge to surface waters or reuse. For processing plants without NPDES permits (i.e., indirect dischargers), wastewater that contains diluted FCS material is collected and treated by the facility. Wastewater treated at processing facilities is then directed through sanitary sewer systems into POTWs for standard wastewater treatment before movement into aquatic environments (i.e., surface water).

9) Brines, Sauces, Marinades for Meat and Poultry

In a typical marinade operation, a fresh marinade batch containing the FCS may be made prior to each 4-hour interval of an 8 hour shift, and then disposed after 4 hours of use. The marinade batches are commonly blended in 50-200 gallon tanks. Following each 4-hour interval, the remainder of the marinade batch, typically up to 30-40 percent, is treated at the meat or poultry processor's on-site pretreatment facilities before discharge to a POTW or surface waters, depending upon whether the facility has an individual NPDES permit. Therefore, meat and poultry processors discharge their wastewater first to onsite treatment facilities and subsequently to POTWs or discharged directly to surface waters if the facility has an individual NPDES permit. Direct discharge to surface water is considered the worst-case scenario as it does not take into account any further treatment that may occur at a POTW.

The marinade may be treated with the FCS after the batch is initially made and again treated with the FCS after each hour of use in the marinade operation to maintain the target PAA concentration. For each 4-hour interval, the total amount of marinade that may be typically disposed of in an on-site pretreatment facility or wastewater discharge system is 80 gallons based on a 200 gallon marinade batch. For an 8-hour shift, the total amount of marinade containing the FCS that may be disposed of into an on-site pretreatment facility or wastewater discharge system is 160 gallons. For two 8-hour shifts, the total amount of marinade containing the FCS that may be disposed of into an on-site pretreatment facility or wastewater discharge system is 320 gallons. Within a meat or poultry processor's on-site wastewater discharge system, the FCS components would be diluted in a similar manner to other liquid products, then subsequently diluted further upon entry into the POTW and surface waters.

10) Aseptic Packaging

The FCS may be used alone or in combination with other processes in the commercial sterilization of aseptic filling systems and glass and plastic food packaging and their enclosures prior to filling, except for use on food packaging used in contact with infant formula or human milk or on aseptic filling equipment used to fill such packaging. In a typical food processing facility, a fresh batch containing the FCS may be initially made

prior to an eight (8) hour shift, and then completely disposed of after approximately 6 cycles of 8 hours each (48 hours total time) of use. Due to use of the FCS and loss of the FCS during treatment of the glass and plastic food packaging and their enclosures, it is often necessary to replenish the FCS containing reservoirs during the 6 cycles of use. The FCS used for replenishment is typically made at the beginning of an 8-hour shift during the 6 cycles of use. The reservoirs are then filled and re-filled as needed.

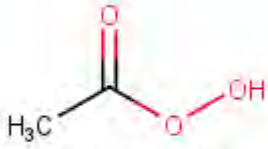
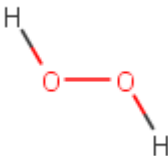
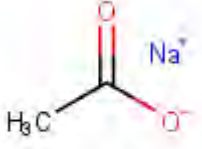
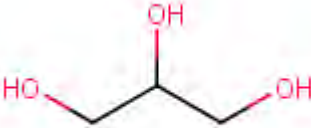
The batches containing the FCS are commonly blended in tanks filled to approximately 900 gallons. Typically, about 600 gallons of the FCS in a reservoir is intended for use in glass and plastic food packaging treatment operations and approximately 300 gallons of the FCS in a reservoir is used in enclosure treatment operations. During each 8-hour shift, the loss of the FCS solution due to its use, may be up to 50 percent or 450 gallons of the FCS. The FCS solution that is lost during use is diluted with other liquid waste products at the processing plant. The diluted FCS solution will be disposed of with processing plant wastewater according to NPDES regulations. For processing plants that hold a NPDES permit (i.e., direct dischargers), the FCS- containing wastewater will be treated on-site before direct discharge to surface waters. For processing plants without such NPDES permits (i.e., indirect dischargers), the FCS containing wastewater would travel through the sanitary sewer system into POTWs for standard wastewater treatment processes before movement into aquatic environments.

The FCS is initially made up at the target PAA concentration. For each 8-hour shift the total amount of FCS that may be typically disposed of in an on-site pretreatment facility or wastewater discharge system is 450 gallons based on a total of 900 gallons of FCS. For two 8-hour shifts consisting of a typical day, the total amount of the FCS that may be disposed is 900 gallons. The FCS solution will be disposed of with processing plant wastewater according to NPDES regulations. For processing plants that hold a NPDES permit (i.e., direct dischargers), the FCS-containing wastewater will be treated on-site before direct discharge to surface waters. For processing plants without such NPDES permits (i.e., indirect dischargers), the FCS containing wastewater would travel through the sanitary sewer system into POTWs for standard wastewater treatment processes before movement into aquatic environments.

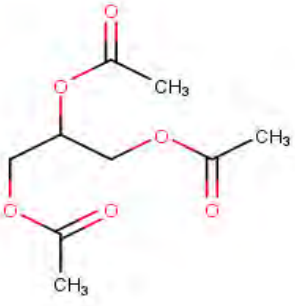
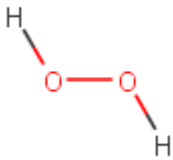
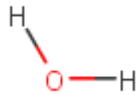
5. Identification of Substances that are Subject of the Proposed Action

This food contact substance is a mixture of peracetic acid, sodium acetate, and glycerin (or glycerol). The FCS is intended to be generated on-site then diluted to achieve the desired active concentration, detailed in Part 4, above.

The chemicals in the proposed FCS include:

Name	Chemical Formula	Chemical Structure	CAS Reg. No.
Peracetic Acid	C ₂ H ₄ O ₃	 Peroxyacetic Acid	79-21-0
Hydrogen Peroxide	H ₂ O ₂		7722-84-1
Sodium Acetate	NaC ₂ H ₃ O ₂	 Sodium Acetate	127-09-3
Glycerin (or Glycerol)	C ₃ H ₈ O ₃	 Glycerol	56-81-5

Clean Chemistry, Inc. supplies the raw materials and hardware used in the on-site generation of the FCS. This includes a source for the chemical feedstocks as well as the generator responsible for the mixing of these raw materials and output of the FCS. This on-demand patented process uses the following chemical feedstocks:

Name	Chemical Formula	Chemical Structure	CAS Reg. No.
Triacetin	C ₉ H ₁₄ O ₆		102-76-1
Hydrogen Peroxide	H ₂ O ₂		7722-84-1
Sodium Hydroxide	NaOH		1310-73-2
Water	H ₂ O		7732-18-5

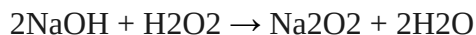
On-demand generation of the FCS eliminates the need to incorporate a stabilizer such as 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) in the formulation. As described below, the FCS is prepared in a non-equilibrium process that produces PAA that is immediately applied in the desired concentration. No stabilizers are contained in this FCS since it is produced and used on-demand.

Ingredients are combined in a controlled process as follows:

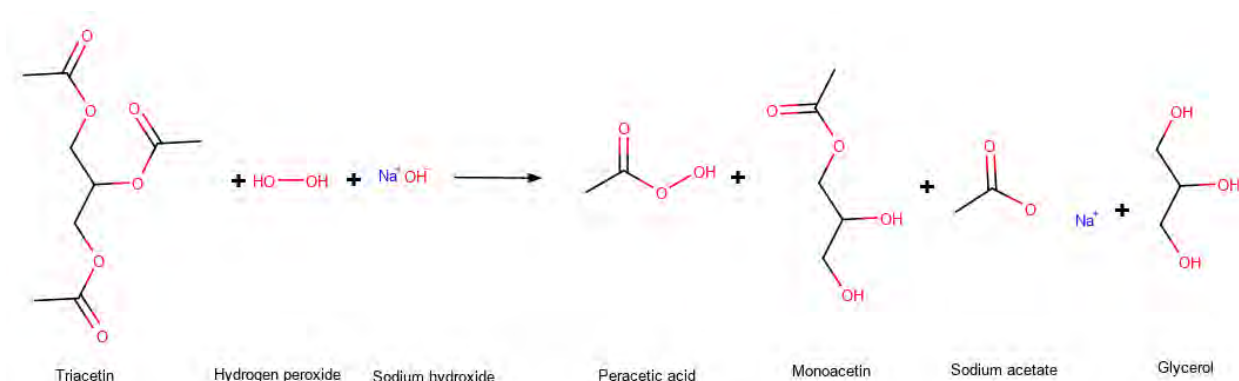
a. Process Step 1: Preparation of the alkaline substrate

Water is fed into the generator/mixer followed by concentrated sodium hydroxide providing the alkaline environment needed for the next steps.

b. Process Step 2: Addition of hydrogen peroxide



Next, hydrogen peroxide is blended into the mixer's alkaline solution and forms an alkaline peroxide solution.

c. Process Step 3: Addition of triacetin

In the next step, under continuous agitation, triacetin is added to the process. Triacetin rapidly reacts with the alkaline peroxide to form an aqueous mixture of PAA. Alkaline pH (pH>10) is used to accelerate the reaction since the hydrogen peroxide anion is a much better nucleophile than hydrogen peroxide. Both the hydrogen peroxide anion, O_2^{2-} and HO^- compete in the reaction with triacetin's acetyl groups, the former producing a PAA and the latter producing acetate. The reaction takes place at ambient temperature and pressure.

The reaction medium that is formed in this step almost instantaneously forms a non-equilibrium solution of PAA. The hydrogen peroxide reacts with triacetin, the acetyl precursor, to form peracetic acid.

d. Process Step 4: Collection of PeroxyMAX

Once generated, PeroxyMAX is collected in a small buffer tank from which it is drawn and conveyed by a chemical feed pump to its point of use immediately after preparation.

6. Introduction of Substances into the Environment**a. Introduction of Substances into the Environment as a Result of Manufacture**

Per 21 CFR Section 25.40(a), the environmental assessment for the FCS should focus on environmental issues only relating to the use and disposal from use of FDA-regulated articles. The FCS is produced on-site and on-demand at the point of use. The FCS is not manufactured in a separate facility and transported to the end-use site, therefore, information on the manufacturing site is not provided here. The end-use site will be the site of manufacture and therefore emissions requirements are addressed in section 6.b. The Notifier confirms that there are no extraordinary circumstances pertaining to the continuous, on-site manufacture of the FCS such as:

- 1) unique emissions that are not already addressed by general or specific emission requirements (including occupational) established by Federal, State or local environmental agencies and that may harm the environment; or,
- 2) an action in violation of Federal, State or local environmental laws or requirements; or,

3) production associated with the proposed action that may adversely affect a species or the habitat of a species as determined under the Endangered Species Act or the Convention on International Trade in Endangered Species of Wild Fauna and Flora to be endangered or threatened, or wild fauna or flora that are entitled to special protection under Federal law.

b. Introduction of Substances into the Environment as a Result of Use/Disposal

Any release of dilute solutions of the FCS into the environment will primarily occur via wastewater treatment systems. Release of the FCS components into the environment will result from its use as spray applications onto food and in processing water. The subsequent disposal of processing water and spray drainage will be to on-site treatment plants and/or POTWs. The total amount of FCS used at a facility will vary depending on the equipment used and the amount of food processed. The maximum use concentration of PAA and HP for each application is as follows:

Summary of Intended Uses

Use	PAA (ppm)	HP (ppm)
Process water or ice used for washing, rinsing, or cooling whole or cut meat, including carcasses, parts, trim, and organs	2000	44.4
Spray, wash, rinse, dip, chiller water, low temperature (e.g., less than 40°F) immersion baths, or scald water for whole or cut poultry carcasses, parts, trim, and organs	2000	44.4
Water, brine, or ice used for washing, rinsing, or cooling processed and pre-formed meat as defined in 21 CFR 170.3(n)(29)	495	11
Water, brine, or ice used for washing, rinsing, or cooling processed and pre-formed poultry as defined in 21 CFR 170.3(n)(34)	495	11
Water for washing or chilling fruits and vegetables in food processing facilities	600	13.3
Water and ice used to commercially prepare fish and seafood	230	5.1
Tempering and before milling of grains of wheat, corn, and rice	6000	133.3
Water for washing shell eggs	2000	44.4
Spray, wash, dip, rinse, mist, or chiller water for hard boiled, peeled eggs	2000	44.4
Additive for liquid, pasteurized whey used in the production of whey protein concentrate	15	0.33
Wash water used to manufacture lactose	30	0.67
Brines, sauces, and marinades applied either on the surface or injected into processed or unprocessed, cooked, or uncooked, whole or cut poultry parts and pieces	50	1.1
Surface sauces and in marinades applied on processed and preformed meat and poultry products	50	1.1
Commercial sterilization of aseptic filling systems and glass and plastic food packaging and their enclosures prior to filling, except for use on food packaging used in contact with infant formula or human milk or on aseptic filling equipment used to fill such packaging	4500	100

Treatment of process water at an on-site wastewater treatment plant or POTW is expected to result in complete degradation of PAA. PAA will break down into oxygen, water, and acetic acid. Any residual hydrogen peroxide remaining in the FCS as an impurity of less than 0.1% will break down into oxygen and water.³ PAA, acetic acid, and hydrogen peroxide are rapidly degraded on contact with organic matter, transition metals, and upon exposure to sunlight. The half-life of PAA in buffered solutions was 63 hours at pH 7 for a 748 ppm solution, and 48 hours at pH 7 for a 95 ppm solution.⁴ The half-life of hydrogen peroxide in natural river water ranged from 2.5 days when initial concentrations were 10,000 ppm, and increased to 15.2 days and 20.1 days when the concentration decreased to 250 ppm and 100 ppm, respectively.⁵ In biodegradation studies of acetic acid using activated sludge, 99% degraded in 7 days under anaerobic conditions.⁶ acetic acid is not expected to concentrate in the wastewater discharged to the wastewater treatment plant or POTW. Therefore, peracetic acid, hydrogen peroxide, and acetic acid are not expected to be introduced into the environment to any significant extent as a result of the proposed use of the FCS.

In the current reaction scheme associated with this FCS, a mixture of hydrogen peroxide is blended with sodium hydroxide and dilution water. Triacetin is then added to this diluted mixture. The resulting reaction converts the three available acetyl groups on triacetin into PAA with a resulting aqueous solution having a PAA purity of greater than 94 percent. The remaining acetyl groups from triacetin would be in the form of monoacetin. None would be in the form of unreacted triacetin or diacetin because the first two acetyl groups are more easily reacted from triacetin than the final acetyl group. Due to excess alkalinity, the ‘first-formed’ PAA hydrolyzes residual monoacetin to sodium acetate and glycerin (or glycerol). To further emphasize that release of monoacetin residuals is not anticipated, and if they were, no significant environmental impacts would result we note that a 2012 U.S. Army Public Health Command study of wildlife toxicity of triacetin⁷ contains the following discussion on page 2:

“When triacetin is released into the environment, it is believed to degrade rapidly. Due to its low vapor pressure of 0.0033 hPa at 25°C, triacetin most likely exists entirely in the vapor phase in the ambient atmosphere (OECD 2002) where it is degraded photochemically to hydroxyl radicals. An estimated K_{oc} of 10.5 suggests that the compound should readily leach from soil to surface water or groundwater. When in water, degradation is expected to occur rapidly and near completely by hydrolysis, producing glycerol and acetic acid, which are further broken down to carbon dioxide. Because of its high solubility and low vapor pressure in a water medium, 99% of the initial parent compound is believed to remain until hydrolysis is complete.”

We assert that monoacetin would behave similarly due to its structural similarity to triacetin. Therefore, release of monoacetin to the environment is not anticipated. As a result, the

³ U.S. Environmental Protection Agency, *Reregistration Eligibility Decision: Peroxy Compounds* (December 1993), p. 18 https://archive.epa.gov/pesticides/reregistration/web/pdf/peroxy_compounds.pdf.

⁴ European Centre for Toxicology and Toxicology of Chemicals, *Joint Assessment of Commodity Chemicals No. 40 Peracetic Acid and its Equilibrium Solutions*, January 2001, p.29, Table 11 <http://www.ecetoc.org/publication/jacc-report-40-peracetic-acid-and-its-equilibrium-solutions/>

⁵ European Centre for Toxicology and Toxicology of Chemicals, *Joint Assessment of Commodity Chemicals No. 22, Hydrogen Peroxide*, January, 1993 p 23, Table 6 www.ecetoc.org/publication/jacc-report-22-hydrogen-peroxide/

⁶ American Chemistry Council, Acetic Acid and Salts Panel, *U.S. High Production (HPV) Chemical Challenge Program: Assessment Plan for Acetic Acid and Salts Category*, June 28, 2001

⁷ U.S. Army Public Health Command “Public Health Notice: Wildlife Toxicity Assessment for Triacetin” (May 2012) https://phc.amedd.army.mil/PHC%20Resource%20Library/WTa_%20Triacetin.pdf

remainder of this EA analysis will consider only the environmental introduction, fate, and impacts of glycerin (or glycerol) and sodium acetate.

7. Fate of Emitted Substances in the Environment

As previously mentioned, PAA, acetic acid, and hydrogen peroxide are not expected to survive treatment at the primary wastewater treatment facilities. Further, no significant amounts of the process residual monoacetin are expected to be released. Therefore, Expected Environmental Concentrations (EECs) have not been calculated for these substances. With respect to the process residuals glycerin (or glycerol) and sodium acetate we provide the subsequent analysis.

The OECD-SIDS document⁸ for glycerol states that 100% of glycerol (or glycerin) will end up in the water phase, and negligible amounts will be distributed towards soil, air and sediment. In addition, it was concluded that glycerol is considered to be readily biodegradable. The OECD-SIDS document also reports that glycerol is 92% biodegradable in 30 days, and more than 60% in 10 days.⁹

Neither the FCS, nor the components used in its generation, are expected to be present in environmentally significant concentrations at discharge or during disposal. Similarly, the already environmentally benign glycerin (or glycerol) and acetic acid byproducts present post-use and at disposal will further degrade into carbon dioxide. Glycerin (or glycerol), acetic acid, and sodium acetate are all readily biodegradable as demonstrated in studies utilizing activated sludge under aerobic conditions. The same studies indicate the estimated concentrations of glycerin (or glycerol), acetic acid, and sodium acetate capable of reaching a wastewater treatment plant to be well below concentrations capable of negative environmental impact. Glycerin (or glycerol) exists almost entirely in the water phase and only negligible amounts would be distributed into soil, air, or sediment.

a. Glycerin (or Glycerol)

Fate in Terrestrial Environment

If released to soil, glycerin (or glycerol) is expected to have very high mobility based upon an estimated Koc of 1. Volatilization from moist soil surfaces is not expected to be an important fate process based upon a Henry's Law constant of 1.73×10^{-8} atm-cu m/mole.¹⁰ Glycerin (or glycerol) may not volatilize from dry soil surfaces based upon its vapor pressure. A 63% of theoretical BOD using activated sludge in the Japanese MITI test suggests that biodegradation is an important environmental fate process in soil and water.

Fate in Aquatic Environment

If released into water, glycerin (or glycerol) is not expected to adsorb to suspended solids and sediment based upon the estimated Koc. Volatilization from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. An

⁸ OECD-SIDS (March 2002) "Glycerol: SIDS Initial Assessment Report" pages 8-9
<https://hvpchemicals.oecd.org/ui/handler.axd?id=4b0a2d87-3183-40d4-84f5-0e118c647b19>

⁹ Ibid.

¹⁰ Ibid.

estimated BCF (bioconcentration factor) of 3 suggests the potential for bioconcentration in aquatic organisms is low. Hydrolysis is not expected to be an important environmental fate process since this compound lacks functional groups that hydrolyze under environmental conditions.

Fate in Air

If released to air, a vapor pressure of 1.68×10^{-4} mm Hg at 25°C indicates glycerin (or glycerol) will exist in both the vapor and particulate phases in the atmosphere. Vapor-phase glycerin (or glycerol) will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 7 hours. Particulate-phase glycerin will be removed from the atmosphere by wet or dry deposition. Glycerin (or glycerol) does not contain chromophores that absorb at wavelengths >290 nm, and therefore is not expected to be susceptible to direct photolysis by sunlight.^{11, 12}

Sodium Acetate

Sodium acetate readily dissociates into sodium cation and the acetate anion; whereby the anion is subsequently biodegraded. Sodium acetate is also inherently biodegradable: 100% after 5 days @ 160 mg/L under aerobic conditions using activated sludge.¹³ Because it is readily biodegradable, it is expected that the environmental concentrations will be well below concentrations found to have any negative impact on the environment after discharge from the wastewater treatment plant.

Data also indicate that sodium acetate (acetic acid, sodium salt) photodegrades, although the rate is substantially slower than that of biodegradation. Studies of sodium acetate indicate 6.6% photomineralization after 17 h UV irradiation (> 290 nm).¹⁴

8. Environmental Effects of Released Substances

a. Glycerin (or Glycerol)

Terrestrial Toxicity

If released to soil, glycerin (or glycerol) is expected to undergo rapid biodegradation under aerobic conditions. It is expected to display very high mobility in soil and it is not expected to significantly volatilize to the atmosphere.

Aquatic Toxicity

¹¹ U.S. Army Public Health Command “Public Health Notice: Wildlife Toxicity Assessment for Triacetin” (May 2012) https://phc.amedd.army.mil/PHC%20Resource%20Library/WTa_%20Triacetin.pdf

¹² OECD-SIDS (March 2002) “Glycerol: SIDS Initial Assessment Report” pages 8-9 <https://hpvchemicals.oecd.org/ui/handler.axd?id=4b0a2d87-3183-40d4-84f5-0e118c647b19>

¹³ American Chemistry Council, Acetic Acid and Salts Panel, *U.S. High Production (HPV) Chemical Challenge Program: Assessment Plan for Acetic Acid and Salts Category*, June 28, 2001

¹⁴ Ibid.

Studies indicate glycerin (or glycerol) is of low toxicity to aquatic organisms¹⁵. The lowest reported LC50 for fish is a 24-hour LC50 of >5000 mg/L for Goldfish (*Carassius auratus*). The lowest EC50 for aquatic invertebrates is >10000 mg/L for *Daphnia magna*. Based on this and related data, the Organization for Economic Cooperation and Development (OECD) Screening Information Dataset (SIDS) reports a predicted no-effect concentration (PNEC) of 780 mg/L. We note that the most conservative EEC possible for glycerin (or glycerol), that of a very small fraction of the 6000 ppm PAA solution used for tempering and before milling of grains of wheat, corn, and rice would be orders of magnitude lower than these ecotoxicity endpoints. Thus, significant environmental impacts from residual glycerin (or glycerol) are not anticipated.

Study	Value	Species	Duration
Acute aquatic, fish	> 5,000 mg/L	<i>Carassius auratus</i> (Goldfish)	24 h
Acute aquatic, algae	2,900 mg/L	<i>Microcystis aeruginosa</i>	24 h
Acute aquatic, <i>Daphnia</i>	10,000 mg/L	<i>Daphnia magna</i>	24 h

b. Sodium Acetate

Ecotoxicity data from the High Production Volume Assessment Plan for Acetic Acid and Salts¹⁶ describe these substances as not highly toxic to mammalian or aquatic plant and animal species. Reported 48-hour LC50 values for fathead minnow, rainbow trout, and *Daphnia* are 92-106 ppm, 105 ppm, and 65 ppm, respectively. Toxicity thresholds for *Scenedesmus quadricauda* (4000 ppm), *Anacystis aeruginosa* (90 ppm) and *Entosiphon sulcatum* (78 ppm) are also given. We note again, as with glycerin (or glycerol), amounts of this residual released to the environment are expected to be much lower than these ecotoxicity endpoints and, as such, no significant environmental impacts are expected.

9. Use of Resources and Energy

The use of the FCS will not require additional energy resources for treatment and disposal of waste solution, as the components readily degrade. The raw materials that are used in production of the mixture are commercially-manufactured materials that are produced for use in a variety of chemical reactions and production processes. Energy used specifically for the production of the mixture components is not significant.

10. Mitigation Measures

As discussed above, no significant adverse environmental impacts are expected to result from the use and disposal of the dilutions of antimicrobial product. Therefore, the mixture is not reasonably expected to result in any new environmental issues that require mitigation measures of any kind.

¹⁵ OECD-SIDS (March 2002) "Glycerol: SIDS Initial Assessment Report" pages 23-24
<https://hpcvchemicals.oecd.org/ui/handler.axd?id=4b0a2d87-3183-40d4-84f5-0e118c647b19>

¹⁶ American Chemistry Council, Acetic Acid and Salts Panel, *U.S. High Production (HPV) Chemical Challenge Program: Assessment Plan for Acetic Acid and Salts Category*, June 28, 2001

11. Alternatives to the Proposed Action

No potential adverse environmental effects are identified herein that would necessitate alternative actions to that proposed in this Food Contact Notification. If the proposed action is not approved, the result would be the continued use of the currently marketed antimicrobial agents that the subject FCS would replace. Such action would have no environmental impact. The addition of the antimicrobial agent to the options available to food processors is not expected to increase the use of PAA antimicrobial products.

12. List of Preparers

This Environmental Assessment was prepared for Clean Chemistry Inc. by:

- a. Carl Evenson, Ph.D., Clean Chemistry, Inc.
- b. Conor Pierce, Ph.D., Clean Chemistry, Inc.
- c. Wendy A. McCombie B.Sc., TSG Consulting

13. Certification

The undersigned official certifies that the information provided herein is true, accurate, and complete to the best of her knowledge.

Name: Wendy A. McCombie, TSG Consulting

Title: Agent for Clean Chemistry Inc.

Signature:



Date: February 1, 2024

14. References

American Chemistry Council, Acetic Acid and Salts Panel, *U.S. High Production (HPV) Chemical Challenge Program: Assessment Plan for Acetic Acid and Salts Category*, June 28, 2001

European Centre for Toxicology and Toxicology of Chemicals (ECETOC), *Joint Assessment of Commodity Chemicals (JACC) No. 40, Peracetic Acid and its Equilibrium Solutions*, January 2001.
<http://www.ecetoc.org/publication/jacc-report-40-peracetic-acid-and-its-equilibrium-solutions/>

European Centre for Toxicology and Toxicology of Chemicals (ECETOC), *Joint Assessment of Commodity Chemicals (JACC) No. 22, Hydrogen Peroxide*, January, 1993.
www.ecetoc.org/publication/jacc-report-22-hydrogen-peroxide/

OECD-SIDS (March 2002) "Glycerol: SIDS Initial Assessment Report"
<https://hpvchemicals.oecd.org/ui/handler.axd?id=4b0a2d87-3183-40d4-84f5-0e118c647b19>

U.S. Army Public Health Command “Public Health Notice: Wildlife Toxicity Assessment for Triacetin” (May 2012) https://phc.amedd.army.mil/PHC%20Resource%20Library/WTa_%20Triacetin.pdf

U.S. Environmental Protection Agency, *Reregistration Eligibility Decision: Peroxy Compounds* (December 1993). https://archive.epa.gov/pesticides/reregistration/web/pdf/peroxy_compounds.pdf.

U.S. Environmental Protection Agency, *Technical Development Document for the Final Effluent Limitations Guidelines and Standards for the Meat and Poultry Products Point Source Category* (40 CFR 432), EPA-821R-04-011, September 8, 2004. https://www.epa.gov/sites/production/files/2015-11/documents/meat-poultry-products_tdd_2004_0.pdf

US EPA Meat and Poultry Products Effluent Guidelines, 40 CFR Part 432
<https://www.epa.gov/eg/meat-and-poultry-products-effluent-guidelines>.

U.S. Food and Drug Administration, *Guidance for Industry: Guide to Minimize Microbial Food Safety Hazards of Fresh-cut Fruits and Vegetables*, February 2008.
<https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-guide-minimize-microbial-food-safety-hazards-fresh-cut-fruits-and-vegetables>

CIVIL COVER SHEET

The JS 44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON NEXT PAGE OF THIS FORM.)

I. (a) PLAINTIFFS

EnviroTech Chemical Services, Inc.

(b) County of Residence of First Listed Plaintiff (EXCEPT IN U.S. PLAINTIFF CASES)

(c) Attorneys (Firm Name, Address, and Telephone Number)
Eversheds Sutherland (US) LLP
98 San Jacinto Blvd, Austin, TX, 78701
512-721-2700

DEFENDANTS

Clean Chemistry, Inc.

County of Residence of First Listed Defendant (IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE TRACT OF LAND INVOLVED.

Attorneys (If Known)

II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

- ☐ 1 U.S. Government Plaintiff ☒ 3 Federal Question (U.S. Government Not a Party)
- ☐ 2 U.S. Government Defendant ☐ 4 Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant)

- | | PTF | DEF | | PTF | DEF |
|---|----------------------------|----------------------------|---|----------------------------|----------------------------|
| Citizen of This State | ☐ 1 | ☐ 1 | Incorporated or Principal Place of Business In This State | ☐ 4 | ☐ 4 |
| Citizen of Another State | ☐ 2 | ☐ 2 | Incorporated and Principal Place of Business In Another State | ☐ 5 | ☐ 5 |
| Citizen or Subject of a Foreign Country | ☐ 3 | ☐ 3 | Foreign Nation | ☐ 6 | ☐ 6 |

IV. NATURE OF SUIT (Place an "X" in One Box Only)

Click here for: [Nature of Suit Code Descriptions.](#)

CONTRACT	TORTS	FORFEITURE/PENALTY	BANKRUPTCY	OTHER STATUTES
☐ 110 Insurance ☐ 120 Marine ☐ 130 Miller Act ☐ 140 Negotiable Instrument ☐ 150 Recovery of Overpayment & Enforcement of Judgment ☐ 151 Medicare Act ☐ 152 Recovery of Defaulted Student Loans (Excludes Veterans) ☐ 153 Recovery of Overpayment of Veteran's Benefits ☐ 160 Stockholders' Suits ☐ 190 Other Contract ☐ 195 Contract Product Liability ☐ 196 Franchise	PERSONAL INJURY ☐ 310 Airplane ☐ 315 Airplane Product Liability ☐ 320 Assault, Libel & Slander ☐ 330 Federal Employers' Liability ☐ 340 Marine ☐ 345 Marine Product Liability ☐ 350 Motor Vehicle ☐ 355 Motor Vehicle Product Liability ☐ 360 Other Personal Injury ☐ 362 Personal Injury - Medical Malpractice PERSONAL INJURY ☐ 365 Personal Injury - Product Liability ☐ 367 Health Care/Pharmaceutical Personal Injury Product Liability ☐ 368 Asbestos Personal Injury Product Liability PERSONAL PROPERTY ☐ 370 Other Fraud ☐ 371 Truth in Lending ☐ 380 Other Personal Property Damage ☐ 385 Property Damage Product Liability	☐ 625 Drug Related Seizure of Property 21 USC 881 ☐ 690 Other LABOR ☐ 710 Fair Labor Standards Act ☐ 720 Labor/Management Relations ☐ 740 Railway Labor Act ☐ 751 Family and Medical Leave Act ☐ 790 Other Labor Litigation ☐ 791 Employee Retirement Income Security Act IMMIGRATION ☐ 462 Naturalization Application ☐ 465 Other Immigration Actions	☐ 422 Appeal 28 USC 158 ☐ 423 Withdrawal 28 USC 157 INTELLECTUAL PROPERTY RIGHTS ☐ 820 Copyrights ☒ 830 Patent ☐ 835 Patent - Abbreviated New Drug Application ☐ 840 Trademark ☐ 880 Defend Trade Secrets Act of 2016 SOCIAL SECURITY ☐ 861 HIA (1395ff) ☐ 862 Black Lung (923) ☐ 863 DIWC/DIWW (405(g)) ☐ 864 SSID Title XVI ☐ 865 RSI (405(g)) FEDERAL TAX SUITS ☐ 870 Taxes (U.S. Plaintiff or Defendant) ☐ 871 IRS—Third Party 26 USC 7609	☐ 375 False Claims Act ☐ 376 Qui Tam (31 USC 3729(a)) ☐ 400 State Reapportionment ☐ 410 Antitrust ☐ 430 Banks and Banking ☐ 450 Commerce ☐ 460 Deportation ☐ 470 Racketeer Influenced and Corrupt Organizations ☐ 480 Consumer Credit (15 USC 1681 or 1692) ☐ 485 Telephone Consumer Protection Act ☐ 490 Cable/Sat TV ☐ 850 Securities/Commodities/Exchange ☐ 890 Other Statutory Actions ☐ 891 Agricultural Acts ☐ 893 Environmental Matters ☐ 895 Freedom of Information Act ☐ 896 Arbitration ☐ 899 Administrative Procedure Act/Review or Appeal of Agency Decision ☐ 950 Constitutionality of State Statutes
REAL PROPERTY ☐ 210 Land Condemnation ☐ 220 Foreclosure ☐ 230 Rent Lease & Ejectment ☐ 240 Torts to Land ☐ 245 Tort Product Liability ☐ 290 All Other Real Property	CIVIL RIGHTS ☐ 440 Other Civil Rights ☐ 441 Voting ☐ 442 Employment ☐ 443 Housing/Accommodations ☐ 445 Amer. w/Disabilities - Employment ☐ 446 Amer. w/Disabilities - Other ☐ 448 Education PRISONER PETITIONS Habeas Corpus: ☐ 463 Alien Detainee ☐ 510 Motions to Vacate Sentence ☐ 530 General ☐ 535 Death Penalty Other: ☐ 540 Mandamus & Other ☐ 550 Civil Rights ☐ 555 Prison Condition ☐ 560 Civil Detainee - Conditions of Confinement			

V. ORIGIN (Place an "X" in One Box Only)

- ☒ 1 Original Proceeding ☐ 2 Removed from State Court ☐ 3 Remanded from Appellate Court ☐ 4 Reinstated or Reopened ☐ 5 Transferred from Another District (specify) ☐ 6 Multidistrict Litigation - Transfer ☐ 8 Multidistrict Litigation - Direct File

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing (Do not cite jurisdictional statutes unless diversity):
35 USC 271
Brief description of cause:
Patent Infringement

VII. REQUESTED IN COMPLAINT:

☐ CHECK IF THIS IS A CLASS ACTION UNDER RULE 23, F.R.Cv.P. DEMAND \$ CHECK YES only if demanded in complaint:
JURY DEMAND: ☒ Yes ☐ No

VIII. RELATED CASE(S) IF ANY

(See instructions): JUDGE DOCKET NUMBER

DATE Oct 29, 2024 SIGNATURE OF ATTORNEY OF RECORD /s/ Michael J. Woodson

FOR OFFICE USE ONLY

RECEIPT # AMOUNT APPLYING IFP JUDGE EnviroTech Ex. 2003 Clean Chemistry v. EnviroTech IPR2025-01472 Page 141

INSTRUCTIONS FOR ATTORNEYS COMPLETING CIVIL COVER SHEET FORM JS 44

Authority For Civil Cover Sheet

The JS 44 civil cover sheet and the information contained herein neither replaces nor supplements the filings and service of pleading or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. Consequently, a civil cover sheet is submitted to the Clerk of Court for each civil complaint filed. The attorney filing a case should complete the form as follows:

- I.(a) Plaintiffs-Defendants.** Enter names (last, first, middle initial) of plaintiff and defendant. If the plaintiff or defendant is a government agency, use only the full name or standard abbreviations. If the plaintiff or defendant is an official within a government agency, identify first the agency and then the official, giving both name and title.
- (b) County of Residence.** For each civil case filed, except U.S. plaintiff cases, enter the name of the county where the first listed plaintiff resides at the time of filing. In U.S. plaintiff cases, enter the name of the county in which the first listed defendant resides at the time of filing. (NOTE: In land condemnation cases, the county of residence of the "defendant" is the location of the tract of land involved.)
- (c) Attorneys.** Enter the firm name, address, telephone number, and attorney of record. If there are several attorneys, list them on an attachment, noting in this section "(see attachment)".
- II. Jurisdiction.** The basis of jurisdiction is set forth under Rule 8(a), F.R.Cv.P., which requires that jurisdictions be shown in pleadings. Place an "X" in one of the boxes. If there is more than one basis of jurisdiction, precedence is given in the order shown below.
 United States plaintiff. (1) Jurisdiction based on 28 U.S.C. 1345 and 1348. Suits by agencies and officers of the United States are included here. United States defendant. (2) When the plaintiff is suing the United States, its officers or agencies, place an "X" in this box.
 Federal question. (3) This refers to suits under 28 U.S.C. 1331, where jurisdiction arises under the Constitution of the United States, an amendment to the Constitution, an act of Congress or a treaty of the United States. In cases where the U.S. is a party, the U.S. plaintiff or defendant code takes precedence, and box 1 or 2 should be marked.
 Diversity of citizenship. (4) This refers to suits under 28 U.S.C. 1332, where parties are citizens of different states. When Box 4 is checked, the citizenship of the different parties must be checked. (See Section III below; **NOTE: federal question actions take precedence over diversity cases.**)
- III. Residence (citizenship) of Principal Parties.** This section of the JS 44 is to be completed if diversity of citizenship was indicated above. Mark this section for each principal party.
- IV. Nature of Suit.** Place an "X" in the appropriate box. If there are multiple nature of suit codes associated with the case, pick the nature of suit code that is most applicable. Click here for: [Nature of Suit Code Descriptions](#).
- V. Origin.** Place an "X" in one of the seven boxes.
 Original Proceedings. (1) Cases which originate in the United States district courts.
 Removed from State Court. (2) Proceedings initiated in state courts may be removed to the district courts under Title 28 U.S.C., Section 1441.
 Remanded from Appellate Court. (3) Check this box for cases remanded to the district court for further action. Use the date of remand as the filing date.
 Reinstated or Reopened. (4) Check this box for cases reinstated or reopened in the district court. Use the reopening date as the filing date.
 Transferred from Another District. (5) For cases transferred under Title 28 U.S.C. Section 1404(a). Do not use this for within district transfers or multidistrict litigation transfers.
 Multidistrict Litigation – Transfer. (6) Check this box when a multidistrict case is transferred into the district under authority of Title 28 U.S.C. Section 1407.
 Multidistrict Litigation – Direct File. (8) Check this box when a multidistrict case is filed in the same district as the Master MDL docket.
PLEASE NOTE THAT THERE IS NOT AN ORIGIN CODE 7. Origin Code 7 was used for historical records and is no longer relevant due to changes in statute.
- VI. Cause of Action.** Report the civil statute directly related to the cause of action and give a brief description of the cause. **Do not cite jurisdictional statutes unless diversity.** Example: U.S. Civil Statute: 47 USC 553 Brief Description: Unauthorized reception of cable service.
- VII. Requested in Complaint.** Class Action. Place an "X" in this box if you are filing a class action under Rule 23, F.R.Cv.P.
 Demand. In this space enter the actual dollar amount being demanded or indicate other demand, such as a preliminary injunction.
 Jury Demand. Check the appropriate box to indicate whether or not a jury is being demanded.
- VIII. Related Cases.** This section of the JS 44 is used to reference related pending cases, if any. If there are related pending cases, insert the docket numbers and the corresponding judge names for such cases.

Date and Attorney Signature. Date and sign the civil cover sheet.