peroxycarboxylic acids, the peroxycarboxylic acids must be packed in special containers and shipped under strict Department of Transportation (DOT) guidelines. Further, excess amounts of reagents (*e.g.*, acids, oxidizing agents, and stabilizers) are present in the compositions during shipping to prevent decomposition. For peroxyformic acid, however, the inherent instability of the substance relative to the higher alkyl peracid, and the explosive nature of the substance at the concentrate make it an even more significant challenge to be manufactured, stored and transported before dilution prior to use, in the similar way like higher alkyl peracid. Thus, there are needs for the on-site generation of peroxycarboxylic acids, especially peroxyformic acid.

It is known in the art that peroxycarboxylic acids could be alternatively generated *in situ* through the perhydrolysis of the higher alkyl carboxylic acid esters of polyhydric alcohol, as disclosed in the Patent Application No. WO2012/090124 and U.S. Patent No. 7,919,122. The perhydrolysis reaction, however, has to be carried out under strong alkaline conditions, for example at pH greater than 12, or at least keeping the pH of the solution between 10 to 12 during the perhydrolysis reaction. As a result, the solution has to be acidified after the perhydrolysis reaction in order to bring the generated peroxycarboxylic acid in the form to be efficient as biocide. One approach to increase the perhydrolysis reactivity of the esters is using perhydrolysis enzyme, such as disclosed in U.S. Patent No. 8,865,436. With the help of the enzyme, the reaction could be carried out in close to neutral pH conditions, and thus avoid the acid neutralization process. However, the enzyme itself is expensive, and including the enzyme in the system will also increase the delivery complexity.

There is a need to seek alternative ways to generate peroxycarboxylic acids, namely peroxyformic acids. The present disclosure addresses this and the related needs using, *inter alia*, performic acid.

BRIEF SUMMARY OF THE INVENTION

The present disclosure relates generally to peroxyformic acid forming compositions, methods for forming peroxyformic acid, preferably *in situ*, using the peroxyformic acid forming compositions, the peroxyformic acid formed by the above compositions and methods, and the uses of the peroxyformic acid, preferably *in situ*, for treating a surface or a target. The

present invention further relates to methods for treating a biofilm using peroxyformic acid, including peroxyformic acid generated *in situ*.

In one aspect, the present disclosure is directed to a peroxyformic acid forming composition comprising: a) a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and b) a second reagent that comprises hydrogen peroxide or that comprises a substance that generates hydrogen peroxide when in contact with a liquid, wherein 1) said first reagent and said second reagent are kept separately prior to use, and when it is time to generate peroxyformic acid, said first reagent and said second reagent are configured to be contacted with each other to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of the formed liquid becomes about 8 or lower within about 1 minute after the contact between said first reagent and said second reagent; or 2) said second reagent comprises a substance that generates hydrogen peroxide when in contact with a liquid, said first reagent and said second reagent are comprised in a solid composition, and when it is time to generate peroxyformic acid, said solid composition is configured to be contacted with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of the formed liquid becomes about 8 or lower within about 1 minute after the contact between said solid composition and said liquid.

In another aspect, the present disclosure is directed to a method for forming peroxyformic acid comprising: a) contacting a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and a second reagent that comprises hydrogen peroxide or that comprises a substance that generates hydrogen peroxide when in contact with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, wherein said first reagent and said second reagent are kept separately prior to said contacting and pH of said formed liquid becomes about 8 or lower within about 1 minute after the contact between said first reagent and said second reagent; or b) contacting a solid composition that comprises a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and a second reagent that comprises a substance that generates hydrogen peroxide when in contact with a liquid with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of said formed liquid becomes about 8 or lower within about 1 minute after the contact between said solid composition and said liquid.

In some embodiments, the use of the above peroxyformic acid forming compositions and the above methods for forming peroxyformic acid are at least based on the surprising finding that the formic acid esters of polyhydric alcohol, such as glycerol formates, can quickly or instantly generate peroxyformic acid in the presence of H_2O_2 under very mild pH conditions in the absence of an enzyme. Furthermore, the pH of the solution quickly or instantly moved significantly lower after the mixing of the esters and H_2O_2 solution, thus eliminating the need for adjusting pH of the formed liquid.

In another aspect, the present disclosure is directed to peroxyformic acid formed using the above method.

In an embodiment, the present disclosure is directed to a method for treating a surface or a target, which method comprises a step of contacting a surface or a target with an effective amount of peroxyformic acid formed using the above methods, preferably *in situ*, to form a treated target composition, wherein said treated target composition comprises from about 0.1 ppm to about 10,000 ppm of said peroxyformic acid, and said contacting step lasts for sufficient time to stabilize or reduce microbial population in and/or on said surface or target or said treated target composition.

In another aspect, the present disclosure is directed to a method for treating a target, which method comprises contacting a target with an effective amount of peroxyformic acid as disclosed herein to form a treated target composition, wherein said treated target composition comprises from about 0.1 ppm to about 10,000 ppm of said peroxyformic acid, and said contacting lasts for sufficient time to bleach, remove soils and/or stabilize or reduce microbial population in and/or on said target or said treated target composition.

In another embodiment, the present disclosure is directed to a method for treating a biofilm, which method comprises contacting a biofilm on a surface with an effective amount of peroxyformic acid for a sufficient time to stabilize, reduce and/or remove microbial population in and/or on said treated biofilm, or to stabilize, reduce and/or remove said biofilm on said surface.

While multiple embodiments are disclosed, still other embodiments of the present disclosure will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments of the invention. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates perhydrolysis of various esters according to embodiments of the invention.

The claimed invention is:

1. A peroxyformic acid forming composition comprising:

a) a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and

b) a second reagent that comprises hydrogen peroxide or that comprises a substance that generates hydrogen peroxide when in contact with a liquid,

wherein

1) said first reagent and said second reagent are kept separately prior to use, and when it is time to generate peroxyformic acid, said first reagent and said second reagent are configured to be contacted with each other to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of the formed liquid becomes about 8 or lower within about 1 minute after the contact between said first reagent and said second reagent; or

2) said second reagent comprises a substance that generates hydrogen peroxide when in contact with a liquid, said first reagent and said second reagent are comprised in a solid composition, and when it is time to generate peroxyformic acid, said solid composition is configured to be contacted with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of the formed liquid becomes about 8 or lower within about 1 minute after the contact between said solid composition and said liquid.

2. The peroxyformic acid forming composition of claim 1, wherein the ester comprises glycerol formates, ethylene glycol formates, pentaerythritol formates, mannitol formates, propylene glycol formates, sorbitol formates or sugar formates, wherein the sugar formates comprise sucrose formates, dextrin formates, maltodextrin formates, or starch formates.

3. The peroxyformic acid forming composition of any of claims 1-2, wherein the second reagent has a pH below 11.

4. The peroxyformic acid forming composition of any one of claims 1-3, wherein the first reagent and the second reagent are configured to be contacted with each other to form a solution that has a pH ranging from about 4 to about 9, and comprises peroxyformic acid, or the solid composition is configured to be contacted with a liquid to form a solution that has a pH ranging from about 4 to about 9, and comprises peroxyformic acid, wherein the first reagent and the second reagent are configured to be contacted with each other to form a solution that comprises peroxyformic acid under ambient conditions, or the solid composition is configured to be contacted with a liquid to form a solution that comprises peroxyformic acid under ambient conditions.

5. The peroxyformic acid forming composition of any of claims 1-4, which further comprises a catalyst or an enzyme that catalyzes formation of peroxyformic acid from the ester of a polyhydric alcohol and formic acid, and hydrogen peroxide, and wherein the catalyst or enzyme comprises a perhydrolytic enzyme, lipase, coronase, termanyl or esperease.

6. The peroxyformic acid forming composition of any of claims 1-5, which further comprises a stabilizing agent for peroxyformic acid, a stabilizing agent for hydrogen peroxide, and/or a pH buffering/adjusting agent, and wherein the stabilizing agent is a phosphonate salt(s) and/or a heterocyclic dicarboxylic acid.

7. The peroxyformic acid forming composition of any of claims 1-6, which comprises multiple dosages of the first reagent that are kept separately prior to use, and are used to contact hydrogen peroxide sequentially, and wherein the multiple dosages of the first reagent comprise the same ester of a polyhydric alcohol and formic acid or different esters of polyhydric alcohols and formic acid.

8. The peroxyformic acid forming composition of any of claims 1-7, which comprises in the formed liquid from about 1 ppm to about 500,000 ppm of an ester of a polyhydric alcohol and formic acid, or

wherein the solid composition comprises from about 1 ppm to about 500,000 ppm of an ester of a polyhydric alcohol and formic acid in the formed liquid, and which comprises in the formed liquid about 0.1 ppm to about 300,000 ppm of hydrogen peroxide or a substance at an amount that generates from about 0.1 ppm to about 300,000 ppm of hydrogen peroxide upon contact with a liquid, or wherein the solid composition comprises a substance at an amount that generates from about 0.1 ppm to about 100,000 ppm of hydrogen peroxide in the formed liquid.

9. The peroxyformic acid forming composition of any of claims 1-8, which is configured to form a solution that comprises from about 0.1 ppm to about 10,000 ppm of peroxyformic acid in the formed liquid.

10. The peroxyformic acid forming composition of any of claims 1-9, which is configured to form a solution that comprises at least about 1 ppm peroxyformic acid within about 1 minute of the contact time, and/or which is configured to form a solution that comprises at least about 80% of the peak concentration of peroxyformic acid within from about 5 minutes to about 15 minutes of the contact time, and/or wherein the formed peroxyformic acid maintains at least about 50% of the peak concentration from about 5 minutes to about 25 minutes after the contact between the first reagent and the second reagent.

11. The peroxyformic acid forming composition of any of claims 1-10, which further comprises a C_2-C_{22} percarboxylic acid, and wherein the first reagent, the second reagent or the solid composition comprising the first reagent and the second reagent are kept separately from the C_2-C_{22} percarboxylic acid prior to use.

12. A method for forming peroxyformic acid comprising:

a) contacting a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and a second reagent that comprises hydrogen peroxide or that comprises a substance that generates hydrogen peroxide when in contact with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, wherein said first reagent and said second reagent are kept separately prior to said contacting and pH of said formed liquid becomes about 8 or lower within about 1 minute after the contact between said first reagent and said second reagent; or

b) contacting a solid composition that comprises a first reagent that comprises an ester of a polyhydric alcohol and formic acid, and a second reagent that comprises a substance that generates hydrogen peroxide when in contact with a liquid with a liquid to form a liquid that comprises peroxyformic acid and has a pH below about 11, and pH of said formed liquid becomes about 8 or lower within about 1 minute after the contact between said solid composition and said liquid.

13. The method of claim 12, wherein the ester comprises glycerol formates, ethylene glycol formates, pentaerythritol formates, mannitol formates, propylene glycol formates, sorbitol formates or sugar formates, and wherein the sugar formates are sucrose formates, dextrin formates, maltodextrin formates, or starch formates.

14. The method of any of claims 12-13, wherein the second reagent has a pH ranging from about 0 to about 11, or from about 5 to about 9, and wherein the first reagent and the second reagent are contacted with each other to form a solution that has a pH ranging from about 4 to about 9, and comprises peroxyformic acid, or the solid composition is contacted with a liquid to form a solution that has a pH ranging from about 4 to about 9, and comprises peroxyformic acid.

15. The method of any of claims 12-14, wherein the first reagent and the second reagent are contacted to form a solution that comprises peroxyformic acid under ambient conditions, or the solid

composition is contacted with a liquid to form a solution that comprises peroxyformic acid under ambient conditions.

16. The method of any of claims 12-15, wherein the first reagent and the second reagent are contacted with each other or the solid composition is contacted with a liquid in the presence of a catalyst or an enzyme that catalyzes formation of peroxyformic acid from the ester of a polyhydric alcohol and formic acid, and hydrogen peroxide, and wherein the catalyst or enzyme comprises a perhydrolytic enzyme, lipase, coronase, termanyl or esperease.

17. The method of any of claims 12-16, which further comprises using a stabilizing agent for peroxyformic acid, a stabilizing agent for hydrogen peroxide, and/or a pH buffering/adjusting agent, and wherein the stabilizing agent is phosphonate salt(s) and/or a heterocyclic dicarboxylic acid.

18. The method of any of claims 12-17, which comprises contacting hydrogen peroxide with multiple dosages of the first reagent sequentially, wherein the multiple dosages of the first reagent comprise the same ester of a polyhydric alcohol and formic acid, or wherein the multiple dosages of the first reagent comprise different esters of polyhydric alcohols and formic acid.

19. The method of any of claims 12-18, wherein the first reagent in the formed liquid comprises from about 1 ppm to about 500,000 ppm of an ester of a polyhydric alcohol and formic acid, wherein the second reagent in the formed liquid comprises about 0.1 ppm to about 100,000 ppm of hydrogen peroxide, and wherein the reagents form a solution that comprises from about 0.1 ppm to about 100,000 ppm of peroxyformic acid.

20. The method of any of claims 12-19, which is used to form a solution that comprises at least about 1 ppm peroxyformic acid within about 1 minute of the contact time, and/or a solution that comprises

at least about 80% of the peak concentration of peroxyformic acid within from about 5 minutes to about 15 minutes of the contact time, and/or wherein the formed peroxyformic acid maintains at least about 50% of the peak concentration from about 5 minutes to about 25 minutes after the contact between the first reagent and the second reagent.

21. The method of any of claims 12-20, which further comprises forming a C_2-C_{22} percarboxylic acid in the liquid.

22. The method of claim 21, wherein the C_2-C_{22} percarboxylic acid comprises peroxyacetic acid, peroxyoctanoic acid and/or peroxysulfonated oleic acid.

23. Peroxyformic acid formed using a method of any of claims 12-22.

24. A method for treating a target, which method comprises contacting a target with an effective amount of peroxyformic acid of claim 23 to form a treated target composition, wherein said treated target composition comprises from about 0.1 ppm to about 10,000 ppm of said peroxyformic acid, and said contacting lasts for sufficient time to bleach, remove soils and/or stabilize or reduce microbial population in and/or on said target or said treated target composition.

25. The method of claim 24, wherein the target is a surface in need of high level disinfecting, and the method comprises providing an effective amount of peroxyformic acid of claim 23 to the surface in need of treatment to form a treated surface, wherein said treated surface source comprises from about 1 ppm to about 2,000 ppm of said peroxyformic acid.

26. The method of claim 25, wherein the surface is a medical instrument in need of repurposing or reprocessing.

27. The method of claim 26, wherein the medical instrument is an endoscope and the treated surface comprises from about 10 ppm to about 1,000 ppm of the peroxyformic acid.

28. The method of claim 27, wherein the contacting step lasts for about 10 minutes.

29. The method of claims 24-28, wherein the pH of the peroxyformic acid is from 7-8.

30. The method of claim 24, wherein the peroxyformic acid is used at a concentration from about 1 ppm to about 1,000 ppm.

31. The method of claim 24, wherein the peroxyformic acid is used at a concentration from about 10 ppm to about 300 ppm.

32. The method of any of claims 24-31, wherein the peroxyformic acid is applied to the target by means of a spray, a fog, or a foam, or by dipping all or part of the target is dipped in a composition comprising the peroxyformic acid, and wherein the contacting step lasts for at least 10 seconds.

33. The method of any of claims 24-32, wherein the microbial population in and/or on the target or the treated target composition is reduced by at least one $\log_{10}$, at least two $\log_{10}$ or at least three $\log_{10}$

34. The method of any of claims 24-33, wherein the microbial population comprises a prokaryotic microbial population, a bacterial population, an archaeal population, a eukaryotic microbial population, or combinations thereof.

35. The method of any of claims 24-34, which is conducted at a temperature ranging from about 0°C to about 70°C.

36. The peroxyformic acid forming composition of any of claims 1-11, which does not comprise a perhyrolysis enzyme member of family 7 of the carbohydrate esterases (CE-7).

37. The peroxyformic acid forming composition of any of claims 1-11, wherein the contacting step forms a solution that comprises at least about 1 ppm peroxyformic acid within about 45 seconds or less of the contact time, within about 30 seconds or less of the contact time, within about 15 seconds or less of the contact time, or within about 5 seconds or less of the contact time.

38. The peroxyformic acid forming composition of any of claims 1-11, wherein the contacting step forms a solution that comprises at least about 100 ppm peroxyformic acid within about 5 minutes or less of the contact time.

39. The peroxyformic acid forming composition of any of claims 1-11, wherein the contacting step forms a solution that comprises at least about 500 ppm peroxyformic acid within about 5 minutes or less of the contact time.