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**Stabilized bromine solutions, method of making and uses thereof for biofouling control**

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(54) Title: STABILIZED BROMINE SOLUTIONS, METHOD OF MAKING AND USES THEREOF FOR BIOFOULING CONTROL

(57) Abstract: Stabilized bromine solutions are prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

**Stabilized Bromine Solutions, Method of Making and Uses  
Thereof for Biofouling Control**

**REFERENCE TO RELATED PATENT**

This application is a continuation-in-part of co-pending U.S. Serial No. 09/283,122, filed on March 31, 1999.

**FIELD OF THE INVENTION**

This invention relates generally to water treatment and, more particularly, to stabilized bromine solutions, method of making and uses thereof for biofouling control.

BACKGROUND OF THE INVENTION

Sodium hypochlorite has been widely used in a variety of industrial and recreational water systems to control biofouling. However, sodium hypochlorite is unstable and must be provided in a stabilized form. There are several methods known in the art for stabilizing hypochlorite (See, e.g., U.S. Patent Nos. 3,328,294 and 3,767,586).

Bromine is preferred over chlorine for use in water treatment because of its lower volatility and better performance at high pH and amine environments. However, like sodium hypochlorite, sodium hypobromite is unstable in typical storage conditions and must therefore also be provided in a stabilized form. U.S. Patent Nos. 5,683,654 and 5,795,487, as well as the references disclosed therein, teach various methods for stabilizing sodium hypobromite. The '654 and '487 patents disclose batch methods which utilize sodium hypochlorite and sodium bromide as starting materials, followed by the addition of a stabilizer. WO 97/20909 similarly discloses a process which includes a hypobromite formation step followed by a bromine stabilization step. However, a disadvantage associated with this technique is that unstabilized hypobromite is formed in a separate step at a high concentration and pH. It is known

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that unstabilized hypobromite degrades quickly under such conditions to form bromate, a non-biocidal compound that  
5 is very toxic and a suspected carcinogen.

In addition, WO 97/43392 discloses a process that first forms stabilized chlorine compounds and then converts them to stabilized bromine compounds. However, this type of process is limiting because only  
10 hypochlorite-releasing compounds can be used as the oxidizing source.

Therefore, because the demand for stabilized bromine solutions is expected to increase in the future due to its advantages over chlorine, there is a need for other cost-effective methods of making stabilized bromine which can  
15 use a wider range of oxidants.

Accordingly, it would be desirable to provide a method of making a stabilized bromine solution which can be carried out as a batch or continuous process right at  
20 the site of the commercial application. It would also be desirable to develop a method of making a stabilized bromine solution which is flexible and allows a variety of oxidizers to be utilized.

#### SUMMARY OF THE INVENTION

25 In accordance with an aspect of the present invention there is provided a method of making a stabilized bromine solution without adding an alkaline source to adjust the pH of the solution comprising the steps of:

- 30 a. combining a bromine source and a stabilizer to form a mixture; and
  - b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.
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In accordance with another aspect of the present  
5 invention there is provided a method of preventing  
biofouling on the surfaces of equipment in contact  
with an industrial water system which comprises adding to  
the water system an effective biofouling controlling  
amount of a stabilized bromine solution, said solution  
10 having been prepared without adding an alkaline source to  
adjust the pH of the solution by the steps of:

- a. combining a bromine source and a stabilizer to  
form a mixture; and
- 15 b. adding an oxidizer to the mixture, wherein the  
oxidizer is selected from the group consisting  
of chlorine gas, hypochlorous acid and  
hypochlorite salt.

20 The inventive method is economically appealing  
because it can be carried out as a batch or continuous  
process at the commercial application site, thereby  
eliminating the need to store and transport the stabilized  
bromine solutions. The method of preparation is also  
25 flexible and allows for the utilization of a variety of  
oxidizers.

DETAILED DESCRIPTION OF THE INVENTION

5 The present invention is directed to a method of making stabilized bromine solutions. In accordance with this invention, a bromine source and a stabilizer are combined to form a mixture, and then an oxidizer is added to the mixture.

10 The bromine sources which may be used in embodiments of the present invention include hydrobromic acid, and alkali or alkaline earth metal bromides, such as sodium bromide, potassium bromide and lithium bromide.

The stabilizers which may be employed in embodiments of this invention have the chemical formula  $R-NH-R^1$ ,  
15 wherein R and  $R^1$  are selected from the group consisting of  $R^2 CO$ ,  $R^2 SO_2$ ,  $R^2 CF_2$ ,  $R^2 CHF$ , H, OH and  $PO(OH)_2$  and  $R^2$  is an alkyl group or an aromatic group.

Suitable stabilizers include saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides,  
20 biuret, sulfamic acid and its alkali or alkaline earth metal salts, organic sulfamates and melamine. Sulfamic acid and its alkali or alkaline earth metal salts are the most preferred stabilizers.

25 Optionally, other water treatment chemicals, such as tracing compounds, surfactants, corrosion inhibitors and scale inhibitors, can be added to the bromine/stabilizer mixture.

The oxidizers which may be used include chlorine gas,  
30 hypochlorous acid and hypochlorite salt.

The stabilized bromine solutions can be prepared at the site of the commercial application. This eliminates  
5 the need to store and transport the stabilized bromine solutions and thus the need for adding caustic to adjust the pH and extend the shelf life of the solutions. The present invention can be carried out as either a batch or continuous process.

10 It is preferred that the molar ratio between the bromine source and the stabilizer be in the range of about 0.1 to 10. The molar ratio between the bromine source and the oxidizer should preferably be in the range of about 0.2 to 5.

15 The stabilized bromine solutions may be used in a wide variety of commercial applications. These applications include, but are not limited to, the use of a stabilized bromine solution: (1) as the bleaching agent in a method for the laundering of soiled garments in which  
20 the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent; (2) as the oxidizing and biocidal agent in a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control  
25 biofouling; (4) as the oxidizing and biocidal agent in a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface; (5) in a method for the control of biofouling occurring on the  
30 surfaces of equipment in contact with produced oil field

waters; (6) in a method for controlling biofouling in an aqueous system;

(7) in a method for controlling biofouling in pulp and paper manufacturing process water and process chemicals; and (8) in a method for controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream.

In another embodiment, the invention is a method of preventing biofouling on the surfaces of equipment in contact with an industrial water system. The method comprises adding an effective biofouling controlling amount of a stabilized bromine solution to the water system, wherein the solution is prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

The types of industrial water systems in which the stabilized bromine solution may be used to prevent biofouling include, but are not limited to, cooling water systems, sweetwater systems, gas scrubber systems, air washer systems, evaporative condensers, pasteurizers, produce sanitizer streams, fire protection water systems and heat exchanger tubes.

It is preferred that the amount of stabilized bromine solution which is added to the industrial water system be in the range of about 0.1 ppm to about 2000 ppm and preferably in the range of about 0.5 ppm to about 500 ppm, based on available chlorine concentration. The stabilized bromine solution can be added to the water system by any conventional method, i.e., by slug, intermittently or continuously.

EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

Example 1

This example demonstrates the impact of caustic addition. It also illustrates that caustic addition is not needed if the inventive stabilized bromine solutions are prepared and used at the site of the commercial application.

Three stabilized bromine formulations were prepared with the only difference being their caustic contents. The formulations underwent an accelerated thermal degradation test at 135 °F and the product actives were determined by potassium-thiosulfate titration at various times. The half lives of the products were calculated from first order decay curves. As shown below in Table 1, the product half lives indicate that the lower the caustic addition, the shorter the shelf life.

Table 1

Raw material	Formulation (moles)		
	A	B	C
Sodium hydroxide	0.176	0.628	5.808
Sulfamic acid	0.126	0.126	0.126
Water	0.488	0.488	0.488
Sodium hypochlorite	0.09	0.09	0.09
Sodium bromide	0.09	0.09	0.09
Product half life (days)	1.8	41.3	41.3

Example 2

A laboratory experiment was conducted at room temperature (70 °F) by:

1. Preparing a mixture (solution A) of sodium bromide and sodium sulfamate to contain 33.3% wt of sodium bromide and 17.4% of sodium sulfamate in water;
2. Adding 0.76 ml of 10.9% wt (as available chlorine) chlorine bleach to 1000 ml of synthetic cooling water containing 225 ppm (as CaCO<sub>3</sub>) hardness and 125 ppm (as CaCO<sub>3</sub>) total alkalinity (solution B); and
3. Adding 0.241 ml of solution A to solution B to form the final solution.

One milliliter of the final solution was taken at different time points and diluted 100 times in deionized water. The halogen residual concentrations in the diluted solution were determined using Hach's DPD method 80 on a DR-2000 spectrophotometer. Three types of DPD measurements were taken: (1) free halogen residual using free chlorine reagent and read at 20 seconds after the reagent was added to the test solution, (2) total halogen residual using total chlorine reagent, and (3) 3-minute halogen residual using free chlorine reagent and read at 3 minutes after the reagent was added. As discovered by the inventors, the difference between the total halogen residual and 3-minute halogen residual is the concentration of N-chlorosulfamate.

While determining the halogen residual in the solution, another one milliliter of the final solution was taken and added to a flask containing 100 ml of the synthetic cooling water with  $2.4 \times 10^6$  CFU/ml of cooling water mixed culture bacteria. After five minutes of mixing, an aliquot of sample was taken from the flask and neutralized with sodium

bisulfite. The surviving bacterial population was  
 5 enumerated on 3M's aerobic count Petrifilm® media after  
 appropriate dilution. The test results are summarized  
 below in Table 2.

Table 2

Time (minutes)	Halogen residual concentration (ppm as avail. Cl <sub>2</sub> )			Log reduction of bacterial count
	Free halogen	3-minute free	Total halogen	
10	0.56	0.56	0.92	>6.3
30	0.48	0.60	0.91	>6.3
66	0.57	0.66	0.93	>6.3
135	0.63	0.70	0.93	>6.3
180	0.63	0.76	0.95	>6.3

10

The results show the effective biocidal performance  
 of the prepared solution. In addition, the solution was  
 found to be stable and there was no reduction of total  
 halogen residual during the test period while the  
 15 concentration of N-chlorosulfamate decreased with an  
 increase in the N-bromosulfamate concentration.

While the present invention is described above in  
 connection with preferred or illustrative embodiments,  
 these embodiments are not intended to be exhaustive or  
 20 limiting of the invention. Rather, the invention is  
 intended to cover all alternatives, modifications and  
 equivalents included within its spirit and scope, as  
 defined by the appended claims.

It is to be understood that, any prior art  
 25 publication referred to herein does not constitute an  
 admission that the publication forms a part of the common  
 general knowledge in the art, in Australia or any other  
 country.

In the claims which follow and in the preceding  
 30 description of the invention, except where the context

requires otherwise due to express language or necessary  
implication, the word "comprise" or variations such as  
5 "comprises" or "comprising" is used in an inclusive sense,  
i.e. to specify the presence of the stated features but  
not to preclude the presence or addition of further  
features in various embodiments of the invention.

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CLAIMS

1. A method of making a stabilized bromine solution  
5 without adding an alkaline source to adjust the pH of the  
solution comprising the steps of:
- a. combining a bromine source and a stabilizer to  
form a mixture; and
  - b. adding an oxidizer to the mixture, wherein the  
10 oxidizer is selected from the group consisting  
of chlorine gas, hypochlorous acid and hypochlorite salt.
2. The method of claim 1 wherein the bromine source  
is selected from the group consisting of hydrobromic acid,  
15 alkali earth metal bromides and alkaline earth metal  
bromides.
3. The method of claim 1 wherein the stabilizer has  
the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected  
20 from the group consisting of  $R^2 CO$ ,  $R^2 SO_2$ ,  $R^2 CF_2$ ,  $R^2 CHF$ ,  
H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic  
group.
4. The method of claim 1 wherein the stabilizer is  
25 selected from the group consisting of saccharin, urea,  
thiourea, creatinine, cyanuric acids, alkyl hydantoins,  
monoethanolamine, diethanolamine, organic sulfonamides,  
biuret, sulfamic acid and its alkali or alkaline earth  
metal salts, organic sulfamates and melamine.  
30
5. The method of claim 1 wherein the stabilizer is  
selected from the group consisting of sulfamic acid and  
its alkali or alkaline earth metal salts.
- 35 6. The method of any one of the preceding claims  
wherein the molar ratio between the bromine source and the  
stabilizer is in the range of about 0.1 to 10.

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7. The method of any one of the preceding claims wherein the molar ratio between the bromine source and the oxidizer is in the range of about 0.2 to 5.

8. A stabilized bromine solution produced by the method of any one of the preceding claims.

9. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprising using as the bleaching agent the stabilized bromine solution of claim 8.

10. In a method for the manufacture of cellulosic materials in which cellulosic fibres are bleached with an oxidizing agent, the improvement comprising using as the oxidizing agent the stabilized bromine solution of claim 8.

11. In a method for the control biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

12. In a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

13. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprising adding to the produced oil field waters an effective

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biofouling controlling amount of the stabilized bromine solution of claim 8.

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14. A method of controlling biofouling in an aqueous system which comprises adding to the aqueous system an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

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15. A method of controlling biofouling in pulp and paper manufacturing process water and process chemicals which comprises adding to the process water an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

15

16. A method of controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream which comprises adding to the aqueous stream an effective, microbial growth controlling amount of the stabilized bromine solution of claim 8.

20

17. A method of preventing biofouling on the surfaces of equipment in contact with an industrial water system which comprises adding to the water system an effective biofouling controlling amount of a stabilized bromine solution, said solution having been prepared without adding an alkaline source to adjust the pH of the solution by the steps of:

25

30

a. combining a bromine source and a stabilizer to form a mixture; and

b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.

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18. The method of claim 17 wherein the industrial water system is selected from the group consisting of a cooling water system, sweetwater system, gas scrubber system, air washer system, evaporative condenser, pasteurizer, produce sanitizer stream, fire protection water system and heat exchanger tube.
19. The method of either claims 17 or 18 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.1 to about 2000 ppm as available chlorine.
20. The method of either claims 17 or 18 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.5 to about 500 ppm as available chlorine.
21. A method of making a stabilized bromine solution without adding an alkaline source to adjust the pH of the solution as substantially described herein with reference to Example 2.