TABLE II

AOX FORMATION (ppb) IN STABILIZED HALOGEN SOLUTIONS

DOSE (ppm total halogen as chlorine)	ppb AOX Formed from Specified Halogen Source: Stabilized NaOBr	Unstabilized NaOBr	Stabilized NaOCl	Unstabilized NaOCl
1	29	56		
2	52	124	13	118
3	68	174		
4	91	197		

EXAMPLE 3

Antibacterial Activity of Stabilized Sodium Hypobromite

Freshly prepared solutions of stabilized and unstabilized sodium hypobromite were diluted then added to cooling water in order to achieve a one ppm free halogen residual (as chlorine). Sodium hypochlorite was stabilized in the same fashion as described for NaOBr in Example One with the exception that NaBr was directly replaced with distilled water. Stabilized and unstabilized sodium hypochlorite were diluted then added to cooling water at a final concentration of one ppm free halogen residual (as chlorine). The volumes of all solutions needed to achieve a one ppm free halogen residual (as chlorine) was recorded. Following 6 and 21 days of dark storage, identical dilutions of stabilized and unstabilized sodium hypohalite solutions were prepared and the volume originally required for a one ppm free halogen residual (as chlorine) was added to cooling water containing approximately 10^6 *Pseudomonas aeruginosa* cells/mL. Aliquots were extracted at 10 and 30 minutes into cooling water dilution blanks containing a halogen neutralizer (0.05% $Na_2S_2O_3$) then enumerated on tryprone glucose extract agar. Stabilized NaOBr retained its antibacterial activity after storage while the unstabilized form lost its efficacy against *Pseudomonas aeruginosa* (see Table III below). The results were even more dramatic as the storage period increased. This effect was likely due to the disproportionation of the unstable hypobromite ion into the non-biocidal species bromide and bromate. Surprisingly, NaOCl stabilized in the same manner as NaOBr was comparatively ineffective under the conditions tested (Table III).

TABLE III

ANTIBACTERIAL ACTIVITIES OF STABILIZED & UNSTABILIZED HYPOHALITE SOLUTIONS AFTER 6 & 21 DAYS
equivalent volumes initially required to achieve one ppm free halogen added throughout test

	% BACTERIA KILLED: 6 DAYS OF STORAGE CONTACT TIME (MINUTES) 10	6 DAYS, 30	21 DAYS OF STORAGE CONTACT TIME (MINUTES) 10	21 DAYS, 30
stabilized NaOBr	99.9	100	99.8	100
unstabilized NaOBr	99.8	99.7	0.4	6.1
stabilized NaOCl	0	0	0	21.0
unstabilized NaOCl	100	100	100	100

EXAMPLE 4

Depression of Bromate Formation Following Stabilization of Sodium Hypobromite

Hypohalite ions are known to disproportionate into halate and halide under alkaline conditions. Halate ions are undesirable degradants being suspect carcinogens and are under consideration for governmental regulation. The reaction of NaBr with NaOCl can yield significant amounts of bromate in elevated pH environments. Surprisingly, the stabilization of NaOBr with sodium sulfamate greatly minimized bromate formation (see Table IV below). Stabilized and unstabilized sodium hypobromite solutions were prepared as described in Example One. These solutions were stored in the dark at room temperature during the course of the study. Eight month old samples of stabilized and unstabilized NaOBr, both maintained at pH 14, a condition suitable for bromate formation, were assayed for bromate. A Dionex 4000 series gradient ion chromatography system equipped with AG9-SC/AS9-SC columns and a conductivity detector was used to measure the bromate concentration in the samples. The chromatograph was operated according to a method currently under investigation by the EPA for the analysis of bromate in ozonated drinking water. Purified water from an Interlake Water Systems deionization system was used for the preparation of all reagents and standard solutions to prevent contamination.

TABLE IV

BROMATE FORMATION IN STABILIZED & UNSTABILIZED NaOBr SOLUTIONS STORED FOR EIGHT MONTHS

	STABILIZED NaOBr	UNSTABILIZED NaOBr
PERCENT BROMATE	0.004	2.700

As noted above, the pH of these solutions was high which favors bromate formation. However, NaOCl, which contains significant amounts of NaOH, is typically diluted with system water prior to the introduction of the bromide species in most industrial applications. The pH of this diluted system would be lower than the neat NaOCl/NaBr formulation described above theoretically minimizing bromate formation. The available chlorine in a NaOCl sample diluted (1:100) with distilled water was titrated by the DPD-FAS method. A solution of 45% sodium bromide was added to the dilute NaOCl at a molar ratio of 1 Cl_2: 1 Br forming NaOBr. This reaction proceeded for thirty minutes. Then, appropriate volumes of this dilute NaOBr solution were added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as Cl_2) as determined by the DPD-FAS method. Similarly, a dilution of stabilized sodium hypobromite (1:100) was made in distilled water. Dilute stabilized NaOBr was added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as Cl_2) as determined by the DPD-FAS method. Bromate analysis then proceeded in the manner described above. Bromate was not detected in any of the cooling water samples dosed with either stabilized or unstabilized dilute NaOBr at typical use concentrations. These results signify the safety factor for bromate built into the stabilized sodium hypobromite formulation as well as the industrial in situ oxidation of NaBr with dilute NaOCl.

EXAMPLE 5

Use of Stabilized NaOBr Increased the Percentage of Free Residual in a Recirculating Cooling Water System Compared to Other Stabilized Halogen Compounds

A major drawback to some commercial stabilized chlorine products for industrial water treatment is the low percentage of free chlorine residual delivered to the water system. This effect is due to the strength of the chemical bond between the stabilizer, usually a nitrogenous compound, and chlorine. Chloramines, ie. combined chlorine, are weaker microbicides than free chlorine. However, bromamines are considered to be nearly as effective against microorganisms as free bromine. Thus, it is essential to have a high percentage of the total available halogen in the free form when chlorine products are employed. Conversely, this phenomenon is not as crucial when employing stabilized NaOBr. A commercial heating, ventilation and air conditioning ("HVAC") cooling system was sequentially treated with stabilized NaOCl, a bromochloroalkylhydantoin, and finally stabilized NaOBr. There was a low percentage of free chlorine relative to total available halogen present in the stabilized NaOCl treated system (see Table V below). A lower percentage of free halogen was measured when a different stabilization system, an alkylhydantoin, was employed with bromine and chlorine (see Table V below). However, when stabilized NaOBr was fed into this system, the percentage of free available halogen relative to the total residual measured quickly increased (see Table V below). These phenomena imply that less stabilized NaOBr is required to obtain a free available halogen residual than the equivalent mount of stabilized NaOCl.

TABLE V

Free Residual Oxidant as a Percent of Total Residual Oxidant in Recirculating Cooling Water System

Days in System	Average Free Oxidant as a Percent of Total Residual Oxidant	Biocide Employed
36	13	stabilized NaOCl
45	9	halogenated hydantoins
33	53	stabilized NaOBr

EXAMPLE SIX

Stabilization of Sodium Hypobromite Reduces Volatility

If a biocide is highly volatile, its performance may be adversely affected. For example, the biocide may flash off in the highly aerated conditions of a cooling tower or an air washer. This would lower the biocide concentration in the cooling water wasting the product. Halogen volatility also leads to vapor-phase corrosion of susceptible equipment surfaces. In addition, halogen volatility may cause worker discomfort due to the "swimming pool" aroma. Thus, the need for an efficacious oxidizing biocide with low volatility is evident.

Concentrated solutions of either NaOCl, NaOBr, or stabilized NaOBr were added to a beaker. Halogen vapors were detected from the NaOCl and NaOBr solutions. No odors were noticed from the stabilized NaOBr. This is an improvement over existing products by minimizing halogen odors in product storage areas.

Bleach, NaOCl, is not commonly used in air washer systems due to some of the reasons listed above. Once an effective microbial control dose is achieved, the halogen odor may be so overwhelming that workers would not be able to comfortably operate in the treated areas. The low volatilization of stabilized NaOBr overcomes this drawback. Stabilized sodium hypobromite was added at elevated use concentrations to two textile mill air washers in order to investigate its volatility. Then the air was monitored throughout the mill. A Sensidyne air monitoring device outfitted with halogen detection tubes was used to instantaneously detect halogen in the air. The lower detection limit was 50 ppb which is below the Threshold Limit Value-Short Term Exposure Limit for bromine as established by OSHA. In addition, halogen badges were placed throughout textile mills in order to detect halogen vapors over extended periods of time. Neither monitoring system detected any halogen present in the air following the elevated stabilized NaOBr dose. No halogen odors were encountered in either the air washer unit or the return air. The microbial population was enumerated before and after stabilized NaOBr addition. The microbial population following dosing was reduced by greater than one order of magnitude. This example demonstrates the utility of stabilized sodium hypobromite in controlling the bacterial population while adding no halogen odor to the system area.

Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

We claim:

1. A method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution comprising:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

2. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, and calcium hypochlorite.

3. The method according to claim 1, wherein the bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid.

4. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

5. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 1 to about 20% by weight alkali or alkaline earth metal hypobromite.

6. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 4 to about 15% by weight alkali or alkaline earth metal hypobromite.

7. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 1 to about 20% by weight sodium hypobromite.

8. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 4 to about 15% by weight sodium hypobromite.

9. The method according to claim 7, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 8 to about 14.