

DESCRIPTION

Title of Invention

WATER TREATMENT AGENT

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Technical Field

[0001] The present technology relates to a water treatment technology such as a water treatment agent.

10 Background Art

[0002] In various water systems such as a heat storage water system, a pulp and paper step water system, a dust collection water system, and a scrubber water system, for the purpose of obtaining an effect such as biofouling prevention, slime prevention, microbial (for example, bacterial, 15 fungal, or algal) killing, or the like on the inside of a pipe, a filtration membrane, and the like in the water systems, a hypohalous acid (for example, hypochlorous acid or hypobromous acid) is used. As an example, the above-mentioned effect is obtained by causing a hypohalous acid to flow through open circulation cooling water or the like of cooling 20 water. Among such hypohalous acids, hypobromous acid has a higher microbicidal activity than hypochlorous acid, and thus attention is being paid to the use of hypobromous acid in a water system.

[0003] For example, Patent Literature 1 discloses a method for sterilizing water comprising adding a chlorine-based oxidizing agent and 25 a stabilized hypobromous acid composition to water individually, wherein the stabilized hypobromous acid composition comprises a bromine-based

oxidizing agent or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound.

[0004] For example, Patent Literature 2 proposes, in order to control contamination by a microorganism in a water system, a method for
5 preparing a biocide, comprising the steps of: (a) preparing a stabilized alkali metal or alkaline earth metal hypochlorite having a pH of at least 11 by mixing unstabilized sodium hypochlorite with sulfamic acid as a stabilizing agent in an alkali solution; (b) preparing sodium bromide as a bromide ion source; and (c) adding the bromide ion source prepared in
10 step (b) to the stabilized alkali metal or alkaline earth metal hypochlorite prepared in step (a) (see, for example, claim 1 and paragraph [0047]).

[0005] In addition, for example, Patent Literature 3 proposes, as a method of producing a stabilized bromine solution for biofouling control, a method of producing a stabilized bromine solution comprising the steps
15 of: a. combining a sodium bromide solution as a bromine source with a solid sulfamate as a stabilizing agent to form a mixture; b. slowly adding a sodium hypochlorite solution as an oxidizing agent to the mixture; and c. slowly adding a sodium hydroxide solution as an alkali source to the mixture to adjust the pH of the mixture to at least 13 (see, for example,
20 claim 1 and paragraph [0022]).

Citation List

Patent Literature

[0006] PTL1: JP 2016-209837 A
25 PTL2: JP 2005-519089 A
PTL3: JP 2002-540297 A
PTL4: JP 2014-140056 A

Summary

Technical Problem

[0007] A main object of the present technology is to provide a water treatment technology which exhibits an effect of hypobromous acid well when
5 added to a water system.

Solution to Problem

[0008] As a result of a diligent study to solve the above-mentioned problem, the present inventors have found that it is possible to provide a water
10 treatment technology which exhibits an effect of hypobromous acid well when added to a water system, leading to completion of the present technology.

In an aspect, there is provided a method of producing a water treatment agent, comprising mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of a halogen-based
15 oxidizing agent, and preparing the water treatment agent containing a chloramine compound and 1% or more of the bromide salt, wherein

the mixed solution is prepared by adding and mixing the stabilizing agent and the bromide salt into an aqueous solution adjusted to pH 13 or more with the alkali agent before adding the halogen-based oxidizing agent,

20 1.2 to 3 mol of the stabilizing agent is blended per mol of the halogen-based oxidizing agent,

the stabilizing agent is a sulfamic acid compound,

the halogen-based oxidizing agent is hypochlorous acid or a salt thereof,

and

25 a pH of the water treatment agent is 13 or more.

That is, the present technology is as follows.

- [1] A water treatment agent comprising the following components (a) to (c) and having a pH of 10 or more:
- (a) a chloramine compound,
 - (b) a bromide salt, and
 - 5 (c) 1 to 18% by mass of a carboxyl group polymer having a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.
- [2] The water treatment agent according to above [1], wherein a molar ratio of the chloramine compound to the bromide salt is 1:0.1 to 1.0.
- [3] The water treatment agent according to above [1] or [2], wherein the
- 10 water treatment agent is at least any of one for slime control, one for anticorrosion, or one for scale prevention.
- [4] The water treatment agent according to any of above [1] to [3], wherein the (a) chloramine compound and the (b) bromide salt of the

water treatment agent are obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.

[5] The water treatment agent according to any of above [1] to [4],

- 5 wherein the water treatment agent has a total chlorine detection rate after production of 95% or more and a free chlorine content rate in a total chlorine concentration of 0.05% (as Cl_2) or less.

[6] A method of producing a water treatment agent, comprising mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent,

- 10 and a bromide salt, and of an oxidizing agent.

[7] The method of producing a water treatment agent according to above [6], wherein the stabilizing agent is a sulfamic acid compound.

[8] The method of producing a water treatment agent according to above [6] or [7], wherein the oxidizing agent is a chlorine-based oxidizing agent.

- 15 [9] The method of producing a water treatment agent according to any of above [6] to [8], wherein a pH of the mixed solution is 13 or more.

[10] The method of producing a water treatment agent according to any of above [6] to [9], wherein the mixed solution is obtained by mixing a powdered bromide salt as the bromide salt.

- 20 [11] The method of producing a water treatment agent according to any of above [6] to [10], wherein a carboxyl group polymer is further mixed in such a way as to provide 1 to 18% by mass, and a carboxyl group content rate in the carboxyl group polymer is 0.8 g-COOH/g-polymer or less.

[12] A water treatment agent comprising an alkali agent, a chloramine

- 25 compound, and a bromide salt, wherein

a total chlorine detection rate after production is 95% or more, and a free chlorine content rate in a total chlorine concentration is 0.05% (as Cl_2) or less.

[13] The water treatment agent according to above [12], wherein the
5 water treatment agent is obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.

[14] The water treatment agent according to above [13], wherein a pH of the water treatment agent is 13 or more.

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Advantageous Effects of Disclosure

[0009] According to the present technology, it is possible to provide a water treatment technology which exhibits an effect of hypobromous acid well when added to a water system. The effect described here is not
15 necessarily limited, and may be any of the effects described herein.

Brief Description of Drawings

[0010] [Fig. 1] Fig. 1 shows the change over time in the total oxidizing agent concentration in the water system (pH 8 to 9) when each of samples
20 1 to 4 was added. Sample 1: chloramine compound ($\times$), sample 2: chloramine compound + bromide (Δ), sample 3: chloramine compound + carboxyl group polymer ($\square$), and sample 4: chloramine compound + carboxyl group polymer + bromide ($\diamond$). The amount of a carboxyl group of the carboxyl group polymer is 0.77 g-COOH/g-polymer. The
25 concentration when only the chloramine compound was added was set to 100%.

- [Fig. 2] Fig. 2 shows the relationship between the hypobromous acid concentration (%) and the total oxidizing agent concentration (%) in the water system when the carboxyl group content rate (g-COOH/g-polymer) of the carboxyl group polymer in the water treatment agent was varied and each water treatment agent was added to the water system (pH 8 to 9). The concentration of the carboxyl group polymer in the water system was 5 mg-polymer/L and was measured 48 hours after the addition. The hypobromous acid concentration when no carboxyl group polymer was added was set to 100%.
- 10 [Fig. 3] Fig. 3 shows the relationship between the hypobromous acid concentration (%) and the total oxidizing agent concentration (%) in the water system when the carboxyl group content rate (g-COOH/g-polymer) of the carboxyl group polymer in the water treatment agent was varied and each water treatment agent was added to the water system (pH 8 to 15 9). The concentration of the carboxyl group polymer in the water system was 30 mg-polymer/L and was measured 48 hours after the addition. The hypobromous acid concentration when no carboxyl group polymer was added was set to 100%.
- [Fig. 4] Fig. 4 shows the relationship between the carboxyl group polymer concentration (mg/L) and the hypobromous acid concentration (%) in the water system when the content of the carboxyl group polymer in the water treatment agent was varied and each water treatment agent was added to the water system (pH 8 to 9). The hypobromous acid concentration when no carboxyl group polymer was added was set to 20 100%.
- 25 [Fig. 5] Fig. 5 shows the change over time in the hypobromous acid concentration (mg/L as Cl_2) in the water system when the water

treatment agent of the present technology was added to the water system (pH 8 to 9).

[Fig. 6] Fig. 6 shows the change in the total chlorine detection rate (%) in each water treatment agent of Test Example 29 (Example 1) and Test
5 Examples 30 and 31 (Comparative Example 1 and Comparative Example 2) when a certain time elapsed after the water treatment agent was produced.

Description of Embodiments

10 [0011] Hereinafter, embodiments of the present technology will be described. It should be noted that the embodiments described below show examples of typical embodiments of the present technology, and the scope of the present technology should not be interpreted as being limited thereby.

15 Herein, the percentage is expressed by mass unless otherwise specified. In addition, the upper limit value and the lower limit value of each numerical value range can be arbitrarily combined as desired.

[0012] <1. Outline of the present technology>

A main object of the present technology is to provide a water
20 treatment technology which exhibits an effect of hypobromous acid well when added to a water system.

Then, the present technology can provide the water treatment technology of a first embodiment according to the present technology and the water treatment technology of a second embodiment according to the
25 present technology. Thereby, it is possible to provide a water treatment technology which exhibits an effect of hypobromous acid well when added to a water system.

[0013] The first embodiment of the present technology can provide, for example, a water treatment agent comprising the following components (a) to (c) and having a pH of 10 or more: (a) a chloramine compound, (b) a bromide salt, and (c) 1 to 18% by mass of a carboxyl group polymer having
5 a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.

According to the first embodiment, it is possible to provide a water treatment technology such as a one-component water treatment agent that can exhibit an effect of hypobromous acid well when added to a
10 water system and also exhibit an agent effect of another compound well.

[0014] The second embodiment of the present technology can provide, for example, a method of producing a water treatment agent comprising mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent, and a
15 water treatment agent obtained by the method, as well as a water treatment agent comprising an alkali agent, a chloramine compound, and a bromide salt, wherein a total chlorine detection rate after production is 95% or more and a free chlorine content rate in a total chlorine concentration is 0.05% (as Cl₂) or less.

20 According to the second embodiment, it is possible to provide a water treatment technology such as a water treatment agent which exhibits an effect of hypobromous acid well when added to a water system and is excellent in the quality stability of the agent.

[0015] Further, the present technology can combine the technologies of
25 the first embodiment and the second embodiment. Thereby, it is possible to provide a water treatment technology which exhibits an effect of hypobromous acid well when added to a water system, and further, the

water treatment technology has the following advantages: being able to be made into a one-component type that can also exhibit an agent effect of another compound well and/or being excellent in the quality stability of the agent.

5 [0016] In addition, the present technology can also be applied to a water treatment apparatus or a water treatment system for which an effect of hypobromous acid is expected. It is also possible to provide a water treatment apparatus or a water treatment system of the present technology configured such that the first embodiment and/or the second
10 embodiment of the present technology can be incorporated into a conventional water treatment apparatus or water treatment system for which an effect of bromous acid is expected, to be practiced. The water treatment apparatus or water treatment system of the present technology preferably includes: a storage apparatus for each component used in the
15 present technology; an apparatus for adding each component or a mixed component; or a mixing apparatus or a pipe for mixing each component (for example, mixing by stirring or convection). The water treatment apparatus or water treatment system of the present technology may further include a control unit or a control apparatus described later. In
20 addition, it is also possible to provide an addition apparatus for adding a water treatment agent or each component of the present technology, or the like.

[0017] In addition, it is also possible to realize the water treatment method which allows an effect of hypobromous acid of the present
25 technology to be exhibited, by using a control unit (for example, a computer) including a CPU for controlling the timing of addition, the amount added, the blending ratio, or the like of each component or the

water treatment agent used in the present technology. In addition, it is also possible to realize the method of the present technology by storing the same as a program in a hardware resource including a recording medium (a nonvolatile memory (a USB memory or the like), an HDD, a CD, or the like) and using the control unit. It is also possible to provide a control apparatus or an addition apparatus that controls the addition of an agent to water to be treated using the control unit. Further, the present technology can also provide a water treatment system or a water treatment apparatus including the control apparatus or the addition apparatus.

[0018] The water treatment technology of the first embodiment according to the present technology and the water treatment technology of the second embodiment according to the present technology will be described in detail below. In addition, in the description of the present technology, overlapping configurations, components, and the like in the first embodiment and the second embodiment will be omitted as appropriate.

[0019] <2. Water treatment agent of first embodiment according to the present technology>

Hereinafter, embodiments of the first embodiment of the present technology will be described. It should be noted that the embodiments described below show examples of typical embodiments of the first embodiment of the present technology, and the scope of the first embodiment of the present technology should not be interpreted as being limited thereby.

[0020] A main object of the first embodiment according to the present technology is to provide a water treatment technology such as a one-

component water treatment agent that can exhibit an effect of hypobromous acid well when added to a water system and also exhibit an agent effect of another compound well.

[0021] In general, a polymer having a carboxyl group (hereinafter, also referred to as a "carboxyl group polymer") is used as an agent for slime control, anticorrosion, scale prevention, or the like, and thus the present inventors expected that when a carboxyl group polymer (for example, a maleic acid-based or acrylic acid-based polymer) is blended into a chloramine compound and a bromide salt to prepare a one-component water treatment agent and this water treatment agent is added to a water system, the agent effect of the carboxyl group polymer can also be exhibited in addition to the effect exhibited well by hypobromous acid.

[0022] However, the present inventors have found that when a water treatment agent in which a carboxyl group polymer is blended in a chloramine compound and a bromide salt is added to a water system, the carboxyl group polymer causes decomposition of hypobromous acid in the water system to progress rapidly, resulting in decrease in stability over time of hypobromous acid in the water system and lack of sustainability of the effect of hypobromous acid (see Fig. 1). However, the present inventors dared to diligently study a one-component water treatment agent that can also exhibit an agent effect of a carboxyl group polymer in addition to the effect exhibited by hypobromous acid in a water system.

[0023] As a result, the present inventors have found that it is possible to obtain a one-component water treatment agent which can cause good stability over time to be obtained when added to a water system by adjusting a characteristic and the content of a carboxyl group polymer in a water treatment agent containing a chloramine compound and a

bromide salt. Then, the present inventors have found that not only the effect of the hypobromous acid can be exhibited well but also the medicinal effect of the carboxyl group polymer can be exhibited well, and completed the present technology.

5 That is, the present technology can adopt the following.

[0024] The first embodiment of the present technology can provide a water treatment agent comprising the following components (a) to (c) and having a pH of 10 or more.

(a) a chloramine compound,

10 (b) a bromide salt, and

(c) 1 to 18% by mass of a carboxyl group polymer having a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.

In addition, the molar ratio of the chloramine compound to the bromide salt is preferably 1:0.1 to 1.0.

15 In addition, the water treatment agent is preferably at least any of one for slime control, one for anticorrosion, or one for scale prevention.

[0025] The water treatment agent of the first embodiment of the present technology contains a chloramine compound and a bromide salt that generate hypobromous acid and further contains a specific amount of

20 a specific carboxyl group polymer, and by adjusting the water treatment agent to an alkaline region, hypobromous acid is unlikely to be generated over time in the water treatment agent although the water treatment agent is a one-component water treatment agent. Thereby, the water treatment agent of the first embodiment of the present technology is

25 excellent in the stability over time of the agent quality, and thus even if the water treatment agent is marketed as a one-component type, the stable quality can be maintained, and even if the one-component water

treatment agent of the first embodiment of the present technology is used in a water system after stored for a certain period of time, a good effect can be expected.

[0026] Further, the water treatment agent of the first embodiment of
5 the present technology contains a specific amount of a specific carboxyl group polymer, and thereby when the water treatment agent of the first embodiment of the present technology is added to a water system, the generation of hypobromous acid in the water system can be controlled. Therefore, the water treatment agent of the first embodiment of the
10 present technology can be controlled so as not to rapidly generate hypobromous acid in a water system in a short period of time. Thus, the water treatment agent of the first embodiment of the present technology can gradually generate hypobromous acid over time in the water system, and thus the effect of hypobromous acid in the water system can be
15 maintained over a longer period of time more sustainably.

As another aspect of the water treatment agent of the first embodiment of the present technology, the water treatment agent can also be used as a sustained-release water treatment agent although the water treatment agent is a one-component agent. Rapid release of
20 hypobromous acid in the water system is likely to lead to corrosion or deterioration in the water system, but the water treatment agent of the first embodiment of the present technology can control the generation rate of hypobromous acid to be slow, and thus corrosion or deterioration in the water system can be reduced, and also an effect (for example,
25 microbial removal action) caused by hypobromous acid can be obtained over a long period of time sustainably. Because of this, it is more beneficial to apply the water treatment agent of the first embodiment of

the present technology to, for example, an open circulation type apparatus having a cooling water system, a heat storage water system, a dust collecting water system, a scrubber water system, or the like.

[0027] Further, the carboxyl group polymer used in the first

5 embodiment of the present technology is a component that can be used in an application such as a slime control agent, an anticorrosive agent, or a scale preventive agent. Because of this, the water treatment agent of the first embodiment of the present technology can exhibit an effect of hypobromous acid well when added to a water system, and can also
10 exhibit well an agent effect of a carboxyl group polymer which is another compound.

[0028] The present inventors have made the following hypothesis about the mechanism by which hypobromous acid is generated in a water system when the water treatment agent of the first embodiment of the
15 present technology is used, and further have been diligently studying the mechanism of action of the first embodiment of the present technology.

The water treatment agent of the first embodiment of the present technology is preferably a one-component agent, and is preferably designed to exist in the form of a chloramine compound in which a
20 sulfamic acid compound and hypochlorous acid are bound (hereinafter, a chloramine compound) and a bromide ion and to contain a specific amount of the specific carboxyl group polymer. In the first embodiment of the present technology, it is important to use a carboxyl group polymer having a characteristic thereof adjusted, and thus the carboxyl group
25 content rate in the carboxyl group polymer is adjusted to a predetermined range. In addition, it is important to contain a specific amount of such a specific carboxyl group polymer in a one-component agent and use the

same in a water system. In the first embodiment of the present technology, it is preferable to adjust the water treatment agent to one in a state in which the pH is increased and an excess amount of sulfamic acid coexists, and thereby a reaction that generates hypobromous acid from the chloramine compound can be controlled so that it rarely occurs.

[0029] Then, when the water treatment agent of the first embodiment of the present technology is added to the water system, the chloramine compound and the bromide salt react with each other to generate sulfamic acid, hypobromous acid, and the like. Thereby, it is possible to exhibit the microbial removal effect or the like of hypobromous acid or the like generated in the water system, and it is also possible to exhibit the medicinal effect of the carboxyl group polymer, which is difficult with the conventional one-component water treatment agent, and further, it is also possible to sustainably exhibit the effect of hypobromous acid.

[0030] <2-(a) Chloramine compound>

The chloramine compound used in the first embodiment of the present technology is not particularly limited, and is preferably, for example, a compound in which a hydrogen atom of the amino group is replaced with a chlorine atom (XNHCl) obtained by reacting hypochlorous acid (HOCl) and a compound having a primary amino group (XNH₂) with each other in the reactions shown in the following reaction equations (1) and (2). This compound has a weak oxidizing action on a metal, a membrane, or the like in the water system, and thus can suppress the progress of corrosion and membrane deterioration, and can be used continuously and/or sustainably in the water system.



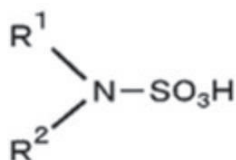
[0031] The chloramine compound used in the first embodiment of the present technology is not particularly limited, and is preferably one generated and obtained by mixing any of a compound having a primary amino group, ammonia, and an ammonium salt (hereinafter, these are
5 also referred to as "NH₂-based compounds") with hypochlorous acid and/or a hypochlorite.

[0032] The compound having a primary amino group is not particularly limited, and examples thereof include an aliphatic amine, an aromatic amine, sulfamic acid, sulfanilic acid, sulfamoylbenzoic acid, and an amino
10 acid. In addition, examples of the ammonium salt include ammonium chloride and ammonium sulfate. One selected from the group consisting of these may be used alone, or two or more may be used by mixing them.

[0033] Among these NH₂-based compounds, sulfamic acid (more preferably NH₂SO₂OH) is preferable. When monochlorosulfamine is
15 generated using sulfamic acid, it becomes a stable chloramine compound.

Examples of the sulfamic acid compound include a compound represented by the following general formula [1] or a salt thereof.

[0034]



...[1]

20 [0035] wherein R¹ and R² are each independently hydrogen or a hydrocarbon having 1 to 8 carbon atoms.

[0036] Examples of such a sulfamic acid compound include N-methylsulfamic acid, N, N-dimethylsulfamic acid, and N-phenylsulfamic acid, in addition to sulfamic acid in which both R¹ and R² are hydrogen.

One selected from the group consisting of these may be used alone, or two or more may be used by mixing them.

[0037] The salt of the compound used in the first embodiment of the present technology is not particularly limited, and examples thereof
5 include an alkali metal salt such as a sodium salt or a potassium salt; an alkaline earth metal salt such as a calcium salt, a strontium salt, or a barium salt; another metal salt such as a manganese salt, a copper salt, a zinc salt, an iron salt, a cobalt salt, or a nickel salt; and an amine salt such as an ammonium salt or a guanidine salt, an amino acid salt or the
10 like; and one selected from the group consisting of these may be used, or two or more may be used in combination as appropriate. Of these, an alkali metal salt (preferably sodium) is preferable from the viewpoint of cost and ease of handling.

These salts can be used as salts of sulfamic acid compounds.

15 [0038] Examples of the sulfamic acid compound used in the first embodiment of the present technology include sodium sulfamate, potassium sulfamate, calcium sulfamate, strontium sulfamate, barium sulfamate, iron sulfamate, and zinc sulfamate. One selected from the group consisting of these may be used alone, or two or more may be used
20 by mixing them.

In the first embodiment of the present technology, one selected from the group consisting of sulfamic acid and these sulfamates can be used alone, or two or more can be used in combination.

[0039] On the other hand, as the hypochlorite to be reacted with the
25 NH_2 -based compound, an alkali metal salt of hypochlorous acid such as sodium hypochlorite; an alkaline earth metal salt of hypochlorous acid such as calcium hypochlorite, or the like can be used. One selected from

the group consisting of these may be used alone, or two or more may be used by mixing them.

[0040] When a NH_2 -based compound and hypochlorous acid and/or a hypochlorite are mixed to generate a chloramine compound, it is

5 preferable from the viewpoint of chloramine generation efficiency and stability to use the NH_2 -based compound and hypochlorous acid and/or the hypochlorite such that the Cl_2/N molar ratio, which is the molar ratio of the effective chlorine (Cl_2) derived from hypochlorous acid and/or the hypochlorite to the nitrogen atom N derived from the NH_2 -based
10 compound, is 0.1 to 1. When the Cl_2/N molar ratio is equal to or less than the above upper limit, the generation of free chlorine can be suppressed, and when the Cl_2/N molar ratio is equal to or more than the above lower limit, it is possible to suppress the lowering of the chloramine generation efficiency relative to the NH_2 -based compound used.

15 [0041] The content of the chloramine compound is, as the lower limit value thereof, preferably 4% by mass or more, more preferably 6% by mass or more, and further preferably 8% by mass or more in the water treatment agent of the first embodiment, and is, as the upper limit value thereof, preferably 24% by mass or less, more preferably 22% by mass or
20 less, and further preferably 20% by mass or less. The numerical value range is preferably 4 to 24% by mass, more preferably 6 to 22% by mass, and further preferably 8 to 20% by mass.

[0042] <2-(b) Bromide salt>

The bromide salt used in the first embodiment of the present
25 technology is not particularly limited, and examples thereof include an alkali metal bromide salt, ammonium bromide salt, an amine

hydrobromide salt, and an amine bromide salt, and one or two or more selected from the group consisting of these can be used.

[0043] Examples of the alkali metal bromide salt include, but are not limited to, sodium bromide, potassium bromide, and lithium bromide.

5 Examples of the amine bromide salt (a linear, branched, cyclic alkyl group or alkenyl group having 1 to 6 carbon atoms) include, but are not limited to, diethylamine hydrobromide, allylamine hydrobromide, cyclohexylamine hydrobromide, monomethylamine hydrobromide, dimethylamine hydrobromide, trimethylamine hydrobromide, normal-
10 butylamine hydrobromide, and ethylamine hydrobromide.

As the bromide salt, one or two or more selected from the group consisting of these can be used.

[0044] The content of the bromide salt is, in terms of bromide, as the lower limit value thereof, preferably 0.1% by mass or more, more
15 preferably 0.5% by mass or more, and further preferably 1.0% by mass or more in the water treatment agent of the first embodiment, and is, as the upper limit value thereof, preferably 10% by mass or less, more preferably 9% by mass or less, and further preferably 8% by mass or less. The numerical value range is preferably 0.1 to 10% by mass, more
20 preferably 0.5 to 9% by mass, and further preferably 1.0 to 8% by mass.

[0045] <Bromide (Br⁻) measurement method>

The concentration of the bromide (Br⁻) in the present technology can be measured by analysis based on the method of JIS-K0101 (1998)
28.4.

25 [0046] <pH measurement method>

The pH in this technology can be measured at an ordinary temperature of 25°C using a general pH meter (for example, "Portable pH

Meter D-54 (pH/mV(ORP)/COND/electrical resistivity/salt/TDS)" or a successor model manufactured by HORIBA, Ltd.).

[0047] <2-(c) Carboxyl group polymer>

5 The carboxyl group polymer used in the first embodiment of the present technology is not particularly limited as long as it is a polymer compound having a specific amount of a carboxyl group.

Then, in the carboxyl group polymer used in the first embodiment of the present technology, it is preferable to set the carboxyl group content rate in the carboxyl group polymer (hereinafter, also referred to as "in the polymer") to a specific rate. Thereby, when the water treatment agent of the first embodiment of the present technology is added to the water system, the action peculiar to the carboxyl group polymer can be developed and without decomposing hypobromous acid generated in the water system very much, the action of hypobromous acid can also be effectively developed.

10 15

[0048] Here, the present inventors have found that by controlling the carboxyl group content rate in the carboxyl group polymer and the carboxyl group concentration in the water system, hypobromous acid in the water system can be controlled not to be decomposed. Further, the present inventors have also found that by studying the relationship between the carboxyl group content rate in the carboxyl group polymer and the carboxyl group polymer concentration in the water system, the content of the carboxyl group polymer contained in the water treatment agent can be specified.

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[0049] Thereby, the present inventors were able to design a one-component water treatment agent containing component (a) a chloramine compound and component (b) a bromide salt, and containing component

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(c) a specific amount of a specific carboxyl group polymer. This water treatment agent is a one-component type, but can suppress decomposition or the like of another component due to a mixed component. This water treatment agent can stably maintain the quality and, when added to a water system, can cause the respective effects of hypobromous acid and the carboxyl group polymer to be exhibited well. Further, by using the specific carboxyl group polymer in a specific amount in a water system, the effect of hypobromous acid can be exhibited sustainably for a longer period of time. For these reasons, the water treatment agent of the first embodiment of the present technology is also excellent from the viewpoint of reduction of the number of times of addition to the water system due to the sustained release properties thereof, the viewpoint of simplification of the work process by using a one-component type, the viewpoint of being able to sustainably develop the effect by reduction of the decomposition of hypobromous acid, the viewpoint of cost reduction, or the like.

[0050] For these reasons, preferably, the carboxyl group polymer of the first embodiment of the present technology has a carboxyl group content rate in the polymer of 0.8 g-COOH/g-polymer or less, and the carboxyl group polymer is in an amount of 1 to 18% by mass in the water treatment agent of the first embodiment.

[0051] [Carboxyl group content rate in polymer]

In the water treatment agent of the first embodiment of the present technology, the content rate of the carboxyl group in the polymer is, as the upper limit value thereof, preferably 0.8 g-COOH/g-polymer or less, more preferably 0.77 g-COOH/g-polymer or less, and further preferably 0.72 g-COOH/g-polymer or less, and is, as the lower limit value thereof, preferably 0.1 g-COOH/g-polymer or more, and more preferably 0.2 g-

COOH/g-polymer or more. The numerical range is more preferably 0.8 to 0.1 g-COOH/g-polymer, and further preferably 0.77 to 0.2 g-COOH/g-polymer.

[0052] <Method of measuring carboxyl group content rate (g-COOH/g-polymer)>

Using ^{13}C -NMR spectrum measurement (carbon-13 nuclear magnetic resonance), carbon derived from a carboxyl group (180 to 182 ppm) can be quantified (measurement temperature of 30°C). Sodium 3-(trimethylsilyl)propionate can be used as a standard substance, and
10 carbon derived from a carboxyl group can be quantified from the sodium 3-(trimethylsilyl)propionate concentration. In addition, the influence of NOE can be removed by gated decoupling (1J (C,H)).

[0053] The content of the carboxyl group polymer in the water treatment agent of the first embodiment is, as the lower limit value
15 thereof, preferably 0.5% by mass or more, more preferably 0.75% by mass or more, and further preferably 1.0% by mass or more, and more preferably 1.5% by mass or more, and is, as the upper limit value thereof, preferably 25% by mass or less, more preferably 20% by mass or less, further preferably 18% by mass or less, and more further preferably 15%
20 by mass or less. The numerical range is preferably 0.5 to 25% by mass, more preferably 0.75 to 20% by mass, and further preferably 1 to 18% by mass from the viewpoint of cost, work efficiency, effect exhibition, and the like.

[0054] <Method of measuring weight average molecular weight of
25 water-soluble polymer>

The weight average molecular weight of the water-soluble polymer used in the present technology can be measured by GPC (gel permeation

chromatography) analysis using standard polystyrene as a standard substance (see, for example, Patent Literature 4 (Reference 1): JP 2014-140056 A).

[0055] The type of the carboxyl group polymer used in the first

5 embodiment of the present technology is not particularly limited, and examples thereof include a water-soluble homopolymer and/or copolymer having a carboxyl group, and further specifically, include a maleic acid-based polymer and a (meth)acrylic acid-based polymer. The "polymer" is meant to include a monopolymer and a copolymer.

10 [0056] More specifically, examples of the carboxyl group polymer include a homomaleic acid polymer, a homo (meth)acrylic acid polymer, a copolymer of a maleic acid or (meth)acrylic acid monomer and an unsaturated monomer copolymerizable therewith, and one, or two or
15 used.

[0057] The carboxyl group polymer in the first embodiment of the present technology preferably contains a maleic acid-based polymer and/or a (meth)acrylic acid-based polymer. The content proportion (content) of the maleic acid-based polymer and/or the (meth)acrylic acid-

20 based polymer in the carboxyl group polymer is preferably 50% by mass or more, more preferably 80% by mass or more, and further preferably 90% by mass or more, more preferably 95% by mass or more, further preferably 99% by mass or more, and more further preferably substantially 100% by mass, and the higher the content proportion in the
25 carboxyl group polymer is, the easier it is to obtain the expected effect of the present technology.

[0058] In addition, examples of the unsaturated monomer copolymerizable with maleic acid or a (meth)acrylic monomer include 2-acrylamide-2-methylpropanesulfonic acid, 2-hydroxy-3-allyloxy-1-propanesulfonic acid, styrenesulfonic acid, vinylsulfonic acid, acrylamide, 5 ethylene, propylene, isopropylene, butylene, isobutylene, hexene, 2-ethylhexene, pentene, isopentene, octene, isooctene, vinyl alcohol, vinyl methyl ether, vinyl ethyl ether, and salts thereof.

Examples include one or two or more polymers selected from the group consisting of a homopolymer, a copolymer, obtained using one or 10 two or more monomers selected from the group consisting of the monomers described above, copolymer(s) of the monomer(s) and isobutylene, and the like.

[0059] When an agent effect such as anticorrosion action is expected, the carboxyl group polymer has a weight average molecular weight 15 preferably on the order of 10^3 to 10^4 and more specifically preferably in the range of 200 to 50,000, more preferably in the range of 500 to 30,000, further preferably in the range of 800 to 30,000, and more preferably in the range of 1,000 to 20,000. The weight average molecular weight is preferably 500 or more in order to obtain an agent effect such as 20 anticorrosion effect, and the weight average molecular weight is preferably 20,000 or less, and more preferably 16,000 or less so that the viscosity of the aqueous solution is low from the viewpoint of handleability.

The weight average molecular weight of the carboxyl group polymer 25 can be measured by the <Method of measuring weight average molecular weight of water-soluble polymer> described above.

[0060] The amount of the carboxyl group polymer added to the water system is preferably an amount such that the concentration in the water system is 1 to 100 mg-polymer/L, more preferably an amount such that the concentration in the water system is 2 to 50 mg-polymer/L, and
5 further preferably an amount such that the concentration in the water system is 5 to 30 mg-polymer, from the viewpoint of obtaining an agent effect such as anticorrosion effect.

[0061] <pH of water treatment agent of first embodiment of the present technology>

10 The pH of the water treatment agent of the first embodiment of the present technology is in the alkaline region from the viewpoint of the stability over time of the agent, and is more preferably 10 or more, further preferably 11 or more, more further preferably 12 or more, and more preferably 13 or more. By adjusting the agent to the alkaline
15 region using a pH adjusting agent (particularly an alkali agent), the generation of hypobromous acid in the water treatment agent can be suppressed, and the stability over time can be maintained or enhanced.

[0062] <Content, mass content ratio, and the like of each component in water treatment agent of first embodiment of the present technology>

20 [Molar ratio of the chloramine compound to the bromide salt]

In the water treatment agent of the first embodiment of the present technology, it is preferable to adjust the molar ratio of the chloramine compound to the bromide salt, and when the chloramine compound is 1, the molar ratio of the chloramine compound to the bromide salt is
25 preferably 1:0.05 to 3.0, more preferably 1:0.1 to 1.5, further preferably 1:0.1 to 1.0, and more further preferably 1:0.2 to 1.0.

[0063] In the water treatment agent of the first embodiment of the present technology, the preferable range of the carboxyl group content rate in the polymer is as described in [Carboxyl group content rate in polymer] described above, and is more preferably 0.3 to 0.72 (g-COOH/g-polymer).

The hypobromous acid concentration (%) in the water system is not particularly limited within the preferable range of the carboxyl group content rate in the polymer described above, and in such a way as to be preferably 75% or more, more preferably 80% or more, further preferably 85% or more, and more preferably 90% or more, it is preferable to prepare the water treatment agent of the first embodiment of the present technology or it is preferable to add the water treatment agent of the first embodiment of the present technology or each component used for this.

The total oxidizing agent concentration (%) in the water system is not particularly limited within the preferable range of the carboxyl group content rate in the polymer described above, and in such a way as to be preferably 80% or more, more preferably 85% or more, and further preferably 90% or more, it is preferable to prepare the water treatment agent of the first embodiment of the present technology or add the water treatment agent of the first embodiment of the present technology.

[0064] As described above, the water treatment agent of the first embodiment of the present technology is excellent in stability over time because it has been found that a specific amount of a specific carboxyl group polymer is used. The total oxidizing agent concentration of the water treatment agent of the first embodiment of the present technology after a certain period of time can be set to preferably 98% or more and more preferably 99% or more when stored at 20°C for 20 days, and can be

set to preferably 85% or more and more preferably 90% or more when stored at 50°C for 20 days, in stationary storage in a constant temperature bath.

[0065] In addition, the water treatment agent of the first embodiment of
5 the present technology can obtain excellent sustained release properties by adjusting a characteristic of the carboxyl group polymer, the specific amount thereof used, and the like as described above. The water treatment agent of the first embodiment of the present technology can be adjusted such that the hypobromous acid concentration 48 hours after its
10 addition to the water system is preferably 0.25 to 1.5 mg/L as CL_2 and more preferably 0.5 to 1 mg/L as CL_2 .

[0066] Further, the first embodiment of the present technology can also adopt the technology of the second embodiment of the present technology described later.

15 By combining the technology of the first embodiment and the technology of the second embodiment, a water treatment technology of a one-component type that can exhibit an effect of hypobromous acid well when added to a water system and also exhibit an agent effect of another compound well can be provided, and the water treatment technology of
20 the one-component type has the advantage of being excellent in the quality stability of the agent.

[0067] As an example adopting the technology of the second embodiment of the present technology described later, for example, the (a) chloramine compound and the (b) bromide salt in the first embodiment
25 of the present technology may be a mixture containing the (a) and (b), obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent. By

using the obtained mixture containing the (a) and (b), the water treatment agent of the first embodiment of the present technology can be adjusted to have a total chlorine detection rate after production of 95% or more and a free chlorine content rate in the total chlorine concentration
5 of 0.05% (as Cl₂) or less.

[0068] <2-(d) Optional component of first embodiment of the present technology>

The water treatment agent of the first embodiment of the present technology can be used in combination with an optional agent in a range
10 that does not impair the effect of the present technology. Examples of the optional agent include, but are limited to, an anticorrosive agent (corrosion inhibitor), a scale preventive agent, a slime control agent, a solvent or dispersion medium such as water, a dispersant enzyme, a microbicide, and a defoaming agent, and various agents that can be
15 generally used for water treatment may be used. One or two or more can be appropriately selected from the group consisting of these.

[0069] In addition, the water treatment agent of the first embodiment of the present technology can be obtained by appropriately mixing each component or each agent of the above-mentioned essential components or
20 optional components or the like, and can be produced according to a general method of producing a water treatment agent or the production method of the second embodiment of the present technology described later.

[0070] <Anticorrosive agent (corrosion inhibitor)>

25 Examples of the anticorrosive agent (corrosion inhibitor) other than the carboxyl group polymer described above is not particularly limited,

and an anticorrosive agent for a cooling water system is preferable. An azole such as benzotriazole or tolyltriazole is preferable.

[0071] <Scale preventive agent>

5 The scale preventive agent other than the carboxyl group polymer described above is not particularly limited, and for example, a phosphoric acid-type scale preventive agent and/or a phosphonic acid-type scale preventive agent is known.

[0072] Examples of the scale preventive agent include orthophosphoric acid, sodium tripolyphosphate, sodium hexametaphosphate, 2-phosphono-
10 1,2,4-tricarboxybutane, 1-hydroxyethylidene-1,1-diphosphonic acid, and aminotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid (also known as 1-hydroxyethane-1,1-diylbisphosphonic acid, HEDP), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC). One or two or more selected from the group consisting of these can be
15 used.

[0073] The content of the anticorrosive agent and/or the scale preventive agent in the water treatment agent of the first embodiment of the present technology is not particularly limited, and is preferably 0.5 to 30% by mass and further preferably 1 to 20% by mass.

20 [0074] <2-2. Method of using water treatment agent of first embodiment of the present technology, and water treatment method using the water treatment agent>

As described above, the water treatment agent of the first embodiment of the present technology can be used as at least any of, for
25 example, one for slime control, one for anticorrosion, or one for scale prevention in expectation of also a medicinal effect of the specific carboxyl

group polymer in addition to an effect of hypobromous acid (for example, microbial removal action or slime control action).

[0075] The first embodiment of the present technology can provide use of or a method of using the water treatment agent of the first embodiment
5 of the present technology, and examples of the purpose of use thereof include water treatment in a water system, a sterilization method in a water system, a slime control method in a water system, an anticorrosion method in a water system, or a membrane scale prevention method in a water system.

10 In addition, the first embodiment of the present technology can also provide a water treatment method, a sterilization method, a slime control method, an anticorrosion method, or a scale prevention method involving adding the water treatment agent of the first embodiment of the present technology to a water system. Any configuration overlapping with the
15 configuration described above for the water treatment agent of the present technology will be omitted as appropriate.

[0076] From the viewpoint of stability over time, the pH of the water system in the method of the first embodiment of the present technology is in the alkaline region, and is more preferably 7 to 10 and further
20 preferably 8 to 9.

[0077] In addition, as another aspect of the first embodiment of the present technology, it is possible to provide a water treatment method, a sterilization method, a slime control method, an anticorrosion method, or a scale prevention method involving adding the following components (a)
25 to (c) to a water system at the same time or different times and/or at the same place or different places.

(a) a chloramine compound; (b) a bromide salt; and (c) 1 to 18% by mass of a carboxyl group polymer having a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.

[0078] In the first embodiment of the present technology, the timing of
5 addition of an agent or each component in the water system is not particularly limited, and it may be added at the same time or separately. And/or, the place where the agent or each component is added in the water system is not particularly limited, and it may be added to the same place or a different place. In addition, each of components (a) to (c) may
10 be added to the water system and mixed to exhibit the effect expected in the first embodiment of the present technology, and each of the components may be mixed to be in the form of a water treatment agent and be added to the water system.

[0079] For example, for slime control or scale prevention for a
15 membrane, it is preferable to add the agent before membrane treatment. In addition, for slime control, sterilization, or anticorrosion for a pipe within a water system, the effect of the present technology can be obtained even at any time and any place in the water system.

The target of the first embodiment of the present technology is
20 preferably a cooling water system, and more preferably the cooling water system is a cooling water system including a metal or a metal pipe of a cooling tank, a cooling tower, a heat exchanger, or the like.

[0080] In addition, in the method of the first embodiment of the present technology, the component (a) chloramine compound and the component
25 (b) bromide salt are preferably added in such a way as to have a molar ratio of 1:0.1 to 1.0. The molar ratio can adopt the same configuration as the molar ratio in the water treatment agent.

[0081] In the method of the first embodiment of the present technology, it is preferable to add the component (c) carboxyl group polymer in such a way as to have a predetermined concentration in the water system. The predetermined concentration in the water system is not particularly
5 limited, and is, as the lower limit value thereof, preferably 0.5 mg/L or more, more preferably 1 mg/L or more, and further preferably 2 mg/L or more, and is, as the upper limit value thereof, preferably 500 mg/L or less, more preferably 80 mg/L or less, further preferably 60 mg/L or less, more further preferably 50 mg/L or less, and further preferably 40 mg/L or less.

10 In addition, in the method of the first embodiment of the present technology, the component (c) carboxyl group polymer is added such that the concentration of the component (c) carboxyl group polymer in the water system is preferably 1 to 80 mg/L, more preferably 2 to 60 mg/L, and further preferably 2 to 50 mg/L.

15 [0082] In the first embodiment of the present technology, it may be used as a water treatment agent kit. In the case of the water treatment agent kit, components (a) to (c) may be housed in their respective separate containers, or a two-agent mixed component and one component may be housed in their respective separate containers. In addition, an optional
20 component may be appropriately included in each container. The use of or method of using the water treatment agent kit can be performed in the same manner as the use of or method of using the water treatment agent described above.

[0083] <3. Method of producing water treatment agent and water
25 treatment agent according to second embodiment according to the present technology>

Hereinafter, embodiments for the second embodiment of the present technology will be described. It should be noted that the embodiments described below show examples of typical embodiments of the second embodiment of the present technology, and the scope of the
5 second embodiment of the present technology should not be interpreted as being limited thereby.

[0084] A main object of the second embodiment according to the present technology is to provide a water treatment agent which exhibits an effect of hypobromous acid well when added to a water system and is excellent
10 in the quality stability of the agent.

[0085] As a result of a diligent study by the present inventors, the present inventors have found that for the water treatment agent obtained by mixing an oxidizing agent into a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, even a certain period
15 of time after production, the total chlorine detection rate is maintained high and the free chlorine content rate in the total chlorine concentration is also maintained low. That is, the present inventors have been able to obtain a water treatment agent which exhibits an effect of hypobromous acid well when added to a water system and is excellent in the quality
20 stability of the agent, and completed the present technology.

That is, the present technology can adopt the following.

[0086] The second embodiment of the present technology can provide a method of producing a water treatment agent, comprising mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent,
25 and a bromide salt, and of an oxidizing agent.

The stabilizing agent is preferably a sulfamic acid compound.

The oxidizing agent is preferably a chlorine-based oxidizing agent.

The pH of the mixed solution is preferably 13 or more.

The mixed solution is preferably obtained by mixing a powdered bromide salt as the bromide salt.

In addition, the second embodiment of the present technology can
5 provide a water treatment agent comprising an alkali agent, a chloramine compound, and a bromide salt, wherein a total chlorine detection rate after production is 95% or more, and a free chlorine content rate in a total chlorine concentration is 0.05% (as Cl_2) or less.

10 The water treatment agent of the second embodiment of the present technology is preferably obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.

The pH of the water treatment agent of the second embodiment of
15 the present technology is preferably 13 or more.

[0087] <3-1. Water treatment agent and method of producing the same according to second embodiment of the present technology>

The second embodiment of the present technology can provide a method of producing a water treatment agent, comprising mixing of a
20 mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent. When obtaining a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, the mixing order of the alkali agent, the stabilizing agent, and the bromide salt is such that any thereof may be mixed first, and is
25 not particularly limited.

[0088] In addition, the second embodiment according to the present technology can provide a water treatment agent obtained by mixing an

oxidizing agent into a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt.

In addition, the second embodiment of the present technology can provide a water treatment agent comprising an alkali agent, a stabilizing
5 agent, and a bromide salt, wherein a total chlorine detection rate after production is equal to or higher than a certain level and/or a free chlorine content rate in a total chlorine concentration is equal to or lower than a certain level.

Thereby, it is possible to provide a water treatment agent which
10 exhibits an effect of hypobromous acid well when added to a water system and is excellent in the quality stability of the agent.

[0089] <3-2. Method of producing water treatment agent according to second embodiment of the present technology>

The present inventors have studied a method of preparing a biocide
15 according to Patent Literature 2 (JP 2005-519089 A). Specifically, in Patent Literature 2, a hypochlorite and sulfamic acid are mixed in a sodium hydroxide solution to prepare a hypochlorite solution having a pH of at least 11 or more, and sodium bromide is finally mixed into the solution to obtain a stabilized hypobromite solution as a biocide.

[0090] However, it has been found that when powdered sodium bromide
20 is mixed by the method of preparing a biocide according to Patent Literature 2, hypobromous acid having high oxidizing power and being unstable is generated. The present inventors have noticed that such a decrease in the stability of hypobromous acid tends to reduce the effect of
25 the active component contained in the biocide. As a result of examining the reason therefor by the present inventors, when powdered sodium bromide is added to the hypochlorous acid solution, a concentrated

bromide solution is generated in a part of the solution when the powder is dissolved. The present inventors have considered that when a concentrated part of this bromide solution is generated, it reacts with hypochlorous acid coexisting to generate unstable hypobromous acid.

5 [0091] On the other hand, the present inventors have also studied a method of adding sodium bromide as a liquid instead of a powder in the method of preparing a biocide according to Patent Literature 2, and noticed the following problem: because it is necessary to add sodium bromide and water at the same time to form an aqueous solution, the
10 concentration possible by blending decreases.

[0092] The present inventors have studied a method of producing a stabilized bromine solution for biofouling control according to Patent Literature 3 (JP 2002-540297 A). Specifically, in Patent Literature 3, a stabilized bromine solution is obtained by mixing a sodium bromide
15 solution and a solid sulfamate, and then adding a sodium hypochlorite solution and a sodium hydroxide solution.

[0093] The present inventors have considered that the method of Patent Literature 3 can suppress the generation of hypobromous acid because no concentrated bromide solution is generated in a part of the solution when
20 the solution is prepared. However, in the method of Patent Literature 3, an oxidizing agent is mixed into the aqueous solution containing sodium bromide and sulfamic acid, which lowers the pH of the oxidizing agent. The present inventors have noticed the following problem: when the pH of the oxidizing agent is lowered, an unstable component having high
25 oxidizing power (for example, dichlorosulfamic acid or bromochlorosulfamic acid) is generated, and by this unstable component,

the effect of the active component contained in the stabilized bromine solution is reduced.

[0094] Then, as a result of a further diligent study by the present inventors, in a water treatment agent obtained by using an alkali agent, 5 a stabilizing agent, a bromide salt, and an oxidizing agent, a water treatment agent obtained by mixing the oxidizing agent into a mixed solution obtained by mixing the alkali agent, the stabilizing agent, and the bromide salt was superior, from the overall viewpoint of the total chlorine detection rate, the total chlorine concentration, and the free 10 chlorine content rate in the total chlorine concentration, to the water treatment agents of Patent Literature 2 and Patent Literature 3 as shown in Examples described later. That is, the water treatment agent of the second embodiment of the present technology thus obtained exhibited the effect of hypobromous acid well when added to the water 15 system, and was excellent in the quality stability of the agent.

[0095] Conventionally, as shown in Patent Literature 2 and Patent Literature 3, when producing a water treatment agent containing a chloramine compound and a bromide salt, there has been the following adherence: the order in which the bromide salt is mixed into the solution 20 is first or last. It is considered that this is because a stable chloramine compound can be obtained from the alkali agent-stabilizing agent-oxidizing agent and thus the mixing of these agents is viewed as a single process. The present inventors have been able to break through this conventional adherence, and thus an excellent water treatment agent of 25 the second embodiment of the present technology can be obtained, and the mixing order found cannot be predicted from the prior art.

[0096] That is, the method of producing a water treatment agent according to the second embodiment of the present technology includes mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.

5 Moreover, the method of producing a water treatment agent according to the second embodiment of the present technology has the following advantage: a one-component water treatment agent that can stably maintain the quality of the agent over a long period of time can be obtained.

10 [0097] <Method of measuring free chlorine concentration, combined chlorine concentration, and total chlorine concentration>

In the present technology, the free chlorine concentration, the combined chlorine concentration, and the total chlorine concentration can be measured as the concentrations of Cl_2 by the DPD method using N,N-diethyl-1,4-phenylenediamine shown in JIS K 0400-33-10:1999. In JIS
15 K 0400-33-10:1999, the following definitions are given.

That is, free chlorine is defined as chlorine that is present in the form of hypochlorous acid, a hypochlorite ion, or dissolved chlorine.

Combined chlorine is defined as chlorine that is present in the form of
20 chloroamine, organic chloroamine, or the like, and is not included in the free chlorine and is total chlorine measured by the DPD method. Total chlorine is defined as chlorine that is present in the form of free chlorine, combined chlorine, or both.

[0098] <Total chlorine detection rate (%) and free chlorine content rate
25 (%)>

In the present technology, the "total chlorine detection rate (%)" is the residual rate (%) of the total chlorine concentration that is the active

component in the water treatment agent, and can be calculated from the "measured value (% as Cl_2) of total chlorine concentration in water treatment agent / theoretical value (% as Cl_2) of total chlorine concentration in water treatment agent " $\times 100$ (%). The theoretical value of the total chlorine concentration is a value of the total chlorine concentration that is computationally formed in the water treatment agent when the oxidizing agent and the stabilizing agent are mixed at the time of production.

In addition, in the present technology, the "free chlorine content rate (% (as Cl_2)) in total chlorine concentration" can be calculated from [free chlorine concentration (% as Cl_2) in the water treatment agent / total chlorine concentration (% as Cl_2) in the water treatment agent] $\times 100\%$. [0099] The <Bromide (Br^-) measurement method> and <pH measurement method> in the second embodiment can be performed in the same manner as the <Bromide (Br^-) measurement method> and <pH measurement method> described in the first embodiment described above. [0100] <2-2-1. Raw materials (alkali agent, stabilizing agent, bromide salt, and oxidizing agent)>

The alkali agent, stabilizing agent, bromide salt, and oxidizing agent used as raw materials in the production method of the second embodiment of the present technology are as follows.

[0101] <3-2-1 (a) Alkali agent>

The alkali agent used in the second embodiment of the present technology is not particularly limited, and examples thereof include basic inorganic salts and basic organic salts.

Examples thereof include alkali metals (for example, lithium, sodium, and potassium), alkaline earth metals (for example, calcium,

magnesium, and barium), salt oxides (for example, sodium oxide and calcium oxide), salt hydroxides (for example, sodium hydroxide, potassium hydroxide, magnesium hydroxide, and calcium hydroxide), carbonates (sodium carbonate, potassium carbonate, and calcium carbonate), and one or two or more selected from the group consisting of these can be used.

The oxides, salt hydroxides, and carbonates are preferably those of an alkali metal or an alkaline earth metal. One or two or more selected from the group consisting of these may be used.

[0102] Among the alkali agents, basic inorganic salts are preferable, and among the basic inorganic salts, salt hydroxides are more preferable from the viewpoint of workability and cost. Among the salt hydroxides, alkali metal hydroxides such as sodium hydroxide and potassium hydroxide are more preferable, and from the viewpoint of cost, sodium hydroxide is further preferable.

[0103] The acidic agent for adjusting the pH of the water treatment agent of the second embodiment of the present technology is not particularly limited, and examples thereof include an acidic inorganic salt and an acidic organic salt. Examples thereof include citric acid, phosphoric acid, tartaric acid, acetic acid, boric acid, phthalic acid, maleic acid, and succinic acid, and one or more selected from the group consisting of these can be used.

[0104] <3-2-1 (b) Stabilizing agent>

The stabilizing agent used in the second embodiment of the present technology is not particularly limited, and is preferably a chlorine stabilizing agent that generates a combined chlorine agent by reaction with an oxidizing agent (preferably an inorganic chlorine agent).

Examples of the chlorine stabilizing agent include any of a compound having a primary amino group, ammonia, and an ammonium salt (hereinafter, these are also referred to as "NH₂-based compounds"), and one or two or more selected from these can be used.

5 The compound having a primary amino group is not particularly limited, and examples thereof include an aliphatic amine, an aromatic amine, sulfamic acid, sulfanilic acid, sulfamoylbenzoic acid, and an amino acid, and one or two or more selected from the group consisting of these can be used.

10 In addition, examples of the ammonium salt include ammonium chloride and ammonium sulfate, and one or two or more selected from the group consisting of these can be used.

[0105] More specific examples of the chlorine stabilizing agent include a sulfamic acid compound; isocyanuric acid; a hydantoin such as 5,5'-
15 dimethylhydantoin, urea, biuret, methyl carbamate, ethyl carbamate, an amide compound such as acetamide, nicotinamide, methanesulfonamide, or toluenesulfonamide; an imide compound such as maleimide, succinimide and phthalimide; an amino acid such as glycine, alanine, histidine, or lysine; an amine compound such as methylamine,
20 hydroxylamine, morpholine, piperazine, imidazole, or histamine; ammonia; and an ammonium salt such as ammonium sulfate, and one or more selected from the group consisting of these can be used.

[0106] Among the chlorine-based stabilizing agents, a sulfamic acid compound is preferable from the viewpoint of environmental load and the
25 like, and examples of the sulfamic acid compound include sulfamic acid, a sulfamic acid derivative, and salts thereof, and one or two or more selected from the group consisting of these can be used.

[0107] Among the chlorine stabilizing agents (preferably NH_2 -based compounds), sulfamic acid (more preferably $\text{NH}_2\text{SO}_2\text{OH}$) is preferable. When monochlorosulfamine is generated using sulfamic acid, it becomes a stable chloramine compound, and thus sulfamic acid is preferable.

5 [0108] Examples of the sulfamic acid compound include the compound represented by the general formula [1] shown in the first embodiment of the present technology or a salt thereof.

[0109] The salt of the compound used as the stabilizing agent is not particularly limited, and the "salt of the compound used in the first
10 embodiment of the present technology" described above can be adopted. Of such salts, an alkali metal salt (preferably sodium) is preferable from the viewpoint of cost and ease of handling.

[0110] The sulfamic acid compound used in the second embodiment of the present technology is not particularly limited, and the "sulfamic acid
15 compound used in the first embodiment of the present technology" described above can be adopted.

Of the stabilizing agents, a sulfamate is more preferable.

[0111] <3-2-1 (c) Bromide salt>

The bromide salt used in the second embodiment of the present
20 technology is not particularly limited, and the "bromide salt used in the first embodiment of the present technology" described above can be adopted.

In addition, the alkali metal bromide salt and the amine bromide salt used in the second embodiment of the present technology are not
25 particularly limited, and "the alkali metal bromide salt" and "the amine bromide salt" used in the first embodiment of the present technology" described above can be adopted.

In addition, the form of a bromide salt when mixed into the solution may be either a chloride solution state or a powdered chloride salt state, and it is preferable to use a powdered bromide from the viewpoint of increasing the concentration of the active component.

5 [0112] <3-2-1 (d) Oxidizing Agent>

The oxidizing agent used in the second embodiment of the present technology is not particularly limited, but a halogen-based oxidizing agent is preferable, and the halogen-based oxidizing agent is not particularly limited, but a chlorine-based oxidizing agent is preferable,
10 and this chlorine-based oxidizing agent is preferable from the viewpoint of being able to obtain a chloramine compound by combination with a chlorine-based stabilizing agent.

[0113] The chlorine-based oxidizing agent used in the second embodiment of the present technology is not particularly limited, and
15 examples thereof include chlorine gas, chlorine dioxide, hypochlorous acid or a salt thereof, chlorous acid or a salt thereof, chloric acid or a salt thereof, perchloric acid or a salt thereof, and chlorinated isocyanuric acid or a salt thereof, and one or two or more selected from the group consisting of these can be used.

20 [0114] Of these, specific examples of the salt form are not particularly limited, but include an alkali metal hypochlorite such as sodium hypochlorite or potassium hypochlorite; an alkaline earth metal hypochlorite such as calcium hypochlorite or barium hypochlorite; an alkali metal chlorite such as sodium chlorite or potassium chlorite; an
25 alkaline earth metal chlorite such as barium chlorite; another metal chlorite such as nickel chlorite; an alkali metal chlorate such as ammonium chlorate, sodium chlorate, or potassium chlorate; an alkaline

earth metal chlorate such as calcium chlorate or barium chlorate, and one or two or more selected from the group consisting of these can be used.

[0115] Among the chlorine-based oxidizing agents, one or two or more selected from the group consisting of a hypochlorite, chlorine dioxide, and
5 chlorine gas are preferable, and among these, a hypochlorite is more preferable from the viewpoint of ease of handling.

[0116] <3-2-2. Method of producing water treatment agent according to second embodiment of the present technology>

In the method of producing a water treatment agent according to
10 the second embodiment of the present technology, it is preferable to at least perform mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt (hereinafter, also referred to as a "three-agent mixed solution"), and of an oxidizing agent. Further, it is more preferable to add an oxidizing agent to the three-agent mixed
15 solution and mix them. Mixing the oxidizing agent can be performed with reference to <3-2-2-2. Oxidizing agent mixing step> described later.

[0117] Example 1 of an embodiment in the production method of the second embodiment of the present technology preferably includes at least a step of mixing an oxidizing agent into a mixed solution obtained by
20 mixing an alkali agent, a stabilizing agent, and a bromide salt. The step of mixing an oxidizing agent can be performed in the same manner as <3-2-2-2. Oxidizing agent mixing step> described later.

As the three-agent mixed solution, one prepared in advance may be used, or one prepared on the same production line or another production
25 line may be used. As the three-agent mixed solution, for example, one prepared in <3-2-2-1. Step of preparing mixed solution obtained by

mixing alkali agent, stabilizing agent, and bromide salt> described later can be used.

From the viewpoint of quality stability of the water treatment agent, more preferably, immediately after mixing the three agents, an
5 oxidizing agent is mixed into the three-agent mixed solution to obtain the water treatment agent.

[0118] In addition, in example 2 of an embodiment in the production method of the second embodiment of the present technology, inclusion of a step of preparing a mixed solution obtained by mixing an alkali agent, a
10 stabilizing agent, and a bromide salt, and a step of mixing an oxidizing agent into the three-agent mixed solution is more preferable from the viewpoint of work efficiency and from the viewpoint of easily adjusting the active component in the water treatment agent.

[0119] The solvent of the solution used in the second embodiment of the
15 present technology is not particularly limited as long as it can dissolve the alkali agent, the stabilizing agent, the bromide salt, and the oxidizing agent, and is preferably water from the viewpoint of safety, handleability, and cost. The water may contain another solvent in a range that does not impair the effect of the present technology, but 99% or more of the
20 solvent is preferably water. Examples of the another solvent include a hydrophilic organic solvent, and examples of the hydrophilic organic solvent include a glycol (for example, ethylene glycol or diethylene glycol), a glycol ether (for example, diethylene glycol monomethyl ether), a glyme, a ketone, an ester (for example, methyl acetate), an alcohol (for example,
25 ethanol or aminoethanol), an acid amide (for example, N,N-dimethylacetamide), and among these, a glycol, a glycol ether, an ester,

and an alcohol are preferable. One or two or more selected from the group consisting of these may be used.

[0120] In the production method of the second embodiment of the present technology, the amount of the solvent (preferably water) to be included is not particularly limited, but the solvent is preferably included in the water treatment agent of the second embodiment such that the amount thereof is preferably 5 to 50% by mass and more preferably 10 to 40% by mass.

[0121] As the production conditions of the production method of the second embodiment of the present technology, the production method can be performed with reference to known production conditions, can be carried out, for example, in a batch or continuous process, and can be carried out at a temperature of about 4 to 40°C.

[0122] An example of the method of producing a water treatment agent according to the second embodiment of the present technology will be described below using the production method of example 2 of the embodiment of the present technology, but the production method of the second embodiment of the present technology is not limited by the above description. In addition, in the production method of the second embodiment of the present technology, the step of preparing a three-agent mixed solution can be skipped.

[0123] The production method of example 2 of the embodiment of the second embodiment of the present technology includes a step of preparing a three-agent mixed solution and a step of mixing an oxidizing agent into the mixed solution.

[0124] <3-2-2-1. Step of preparing mixed solution obtained by mixing alkali agent, stabilizing agent, and bromide salt>

In the "step of preparing a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt" (hereinafter, also referred to as the "three-agent mixed solution preparation step") in the production of the second embodiment of the present technology, the order
5 in which each component of the alkali agent, the stabilizing agent, and the bromide salt is mixed is not particularly limited.

[0125] The three-agent mixed solution of the second embodiment of the present technology can be obtained by adding and mixing the three agents of an alkali agent, a stabilizing agent, and a bromide salt at the
10 same time or separately. More specifically, the three agents may be added separately and sequentially, the two agents may be mixed and then the remaining agent may be mixed, or the three agents may be mixed at the same time.

When the three agents are added separately and sequentially, they
15 are added, for example, (1) in order of the alkali agent, the stabilizing agent, and the bromide salt, (2) in order of the alkali agent, the bromide salt, and the stabilizing agent, and (3) in order of the stabilizing agent, the bromide salt, and the alkali agent, (4) in order of the stabilizing agent, the alkali agent, and the bromide salt, (5) in order of the bromide salt, the
20 stabilizing agent, and the alkali agent, or (6) in order of the bromide salt, the alkali agent, and the stabilizing agent.

[0126] In the three-agent mixed solution preparation step of the second embodiment of the present technology, it is preferable to first mix the alkali agent into the solution. As will be described later, the pH of the
25 solution can be adjusted, using an alkali agent, to the alkaline region, specifically, preferably 11 or more, more preferably 12 or more, and more further preferably 13 or more. By adjusting the solution to the alkaline

region, the quality stability of each agent mixed into this solution is also good.

A water treatment agent having excellent quality stability can be obtained by sequentially or appropriately blending agents into the
5 solution adjusted to the alkaline region.

In addition, in the three-agent mixed solution preparation step of the second embodiment of the present technology, it is more preferable to mix the alkali agent, the stabilizing agent, and the bromide salt in the order presented, or the alkali agent, the bromide salt, and the stabilizing
10 agent in the order presented.

[0127] The treatment temperature in the three-agent mixed solution preparation step of the second embodiment of the present technology is not particularly limited, and the step can be performed under a temperature condition of about 4 to 40°C. In addition, as the mixing
15 means in the three-agent mixed solution preparation step, known means (for example, stirring means) that can mix each agent and the solution can be adopted.

[0128] It is preferred to adjust the pH of the three-agent mixed solution prepared using the alkali agent from the viewpoint of maintaining the
20 quality stability of the agents of the water treatment agent of the second embodiment of the present technology. The pH of the three-agent mixed solution is more preferably 10 or more, further preferably 11 or more, more further preferably 12 or more, and more preferably 13 or more. By adjusting the pH of the three-agent mixed solution as described above,
25 the pH of the water treatment agent of the second embodiment of the present technology finally obtained can be set to the alkaline region, thereby making it possible to exhibit the effect of the active component of

the water treatment agent of the second embodiment of the present technology well. In addition, an alkali agent may be appropriately added in a range that does not impair the effect of the present technology in order to adjust the pH of the water treatment agent of the second
5 embodiment.

[0129] In addition, the respective concentrations of the stabilizing agent and the bromide salt contained in the three-agent mixed solution prepared can be adjusted according to the amounts blended described below, from the viewpoint of maintaining the quality stability of the
10 agents of the water treatment agent of the second embodiment of the present technology.

[0130] The amount of the stabilizing agent (preferably a chlorine-based stabilizing agent) added for use in the preparation of the three-agent mixed solution, is not particularly limited, but is preferably 5 to 80%,
15 more preferably 10 to 70%, and further preferably 16 to 60% in the three-agent mixed solution.

[0131] The amount of the stabilizing agent (preferably a chlorine-based stabilizing agent) added for use in the preparation of the three-agent mixed solution, is not particularly limited. When the oxidizing agent is
20 an inorganic chlorine agent, the amount thereof is preferably 1 to 5 mol, more preferably 1 to 4 mol, and further preferably 1.2 to 3 mol per mol of the oxidizing component contained in the inorganic chlorine agent, from the viewpoint of sufficient reactivity in the same. Thereby, the active component can be maintained well even with a one-component water
25 treatment agent.

[0132] The amount of the bromide salt added for use in the preparation of the three-agent mixed solution is not particularly limited, and is

preferably 3 to 50%, more preferably 6 to 40%, and further preferably 12 to 30% in the three-agent mixed solution.

[0133] <3-2-2-2. Oxidizing agent mixing step>

5 In the "step of mixing an oxidizing agent into the three-agent mixed solution" (hereinafter, also referred to as the "oxidizing agent mixing step") in the production of the second embodiment of the present technology, an oxidizing agent is mixed into the solution obtained by mixing an alkali agent, a stabilizing agent, a bromide salt prepared in the earlier step. Thereby, a four-agent mixed solution can be obtained.

10 Then, when the four agents are mixed, the stabilizing agent and the oxidizing agent react to generate a haloamine compound (preferably a chloramine compound), and under the alkaline region, a water treatment agent containing the haloamine compound (preferably a chloramine compound) and a bromide salt can be prepared.

15 [0134] The amount of the oxidizing agent mixed into the three-agent mixed solution is not particularly limited, but is preferably 20 to 55%, more preferably 30 to 55%, and further preferably 40 to 50% in the four-agent mixed solution.

20 In addition, the mixing mass proportion between the three-agent mixed solution and the oxidizing agent is not particularly limited, and that of the oxidizing agent is preferably 0.5 to 1.5 and more preferably 0.7 to 1.3 with that of the three-agent mixed solution being 1.

[0135] The water treatment agent obtained by the production method of the second embodiment of the present technology exhibits the effect of
25 hypobromous acid well when added to a water system, and is excellent in the quality stability of the agent. Further, the one-component agent obtained by the production method can exhibit the effect of interest even

when stored in this one-component state for a long period of time, and can maintain a certain quality.

[0136] The water treatment agent obtained by the production method of the second embodiment of the present technology contains an alkali agent,
5 a haloamine compound (preferably a chloramine compound), and a bromide salt, and as the water treatment agent, one wherein the total chlorine detection rate (%) is maintained at 95% or more and/or the free chlorine concentration is maintained at 0.05% (as Cl_2) or less in the total chlorine concentration for a long period of time is preferable because
10 decrease in the active component concentration after production is suppressed.

[0137] The content of the stabilizing agent in the water treatment agent of the second embodiment of the present technology is adjusted to be, as the lower limit value thereof, preferably 3% or more, more preferably 5%
15 or more, and further preferably 8% or more, and to be, as the upper limit value thereof, preferably 40% or less, more preferably 35% or less, and further preferably 30% or less, and a more preferable numerical range is more preferably 5 to 35%, and further preferably 8 to 30%.

[0138] The content of the bromide salt in the water treatment agent of the second embodiment of the present technology is adjusted to be, as the lower limit value thereof, preferably 1% or more, more preferably 3% or
20 more, and further preferably 6% or more, and to be, as the upper limit value thereof, preferably 25% or less, more preferably 20% or less, and further preferably 15% or less, and a more preferable numerical range is
25 more preferably 3 to 20%, and further preferably 6 to 15%.

[0139] The content of the oxidizing agent in the water treatment agent of the second embodiment of the present technology is adjusted to be, as

the lower limit value thereof, preferably 20% or more, more preferably 30% or more, and further preferably 40% or more, and to be, as the upper limit value thereof, preferably 60% or less, more preferably 55% or less, and further preferably 50% or less, and a more preferable numerical
5 range is more preferably 30 to 55%, and further preferably 40 to 50%.

[0140] The "total chlorine detection rate (%)" in the water treatment agent of the second embodiment is more preferably 96% or more, further preferably 97% or more, and more further preferably 97.5% or more.

The "free chlorine content rate (% (as Cl_2)) in the total chlorine
10 concentration" in the water treatment agent of the second embodiment is more preferably 0.05% or less, and further preferably 0.04% or less.

[0141] The "total chlorine concentration (% as Cl_2)" when the water treatment agent of the second embodiment is used is more preferably 4.1% or more, further preferably 4.2% or more, and more further
15 preferably 4.3% or more. According to the production method of the second embodiment of the present technology, it is considered that production is possible in such a way as to increase the total chlorine concentration (% as Cl_2) in the water treatment agent of the second embodiment to 4.4% to 4.7%, and thus one having a total chlorine
20 concentration of 4.7% or less, 4.6% or less, 4.5% or less, or 4.4% or less as the upper limit value thereof can be obtained.

[0142] In addition, the total chlorine detection rate (%), the total chlorine concentration (% as Cl_2), and the free chlorine content rate in the total chlorine concentration in the water treatment agent of the second
25 embodiment of the present technology are concentrations preferably after the production to when stored for 4 hours and more preferably after the production to when stored for 1 hour from the viewpoint of reducing the

decomposition of the active component to achieve efficient addition to a water system. The water treatment agent of the second embodiment of the present technology is stable with a high total chlorine detection rate and total chlorine concentration up to about 4 hours after production even
5 if not used immediately 0 hours after production. Because of this, it is possible to perform an operation such as transportation without installing a water treatment agent production apparatus in the immediate vicinity of an addition site of the water system. In addition, the water treatment agent obtained by the production method of the second embodiment of the
10 present technology can suppress rapid decrease in the total chlorine detection rate (%) and the total chlorine concentration (% as Cl_2) in the water treatment agent for about 3 months after production, and can suppress rapid increase in the free chlorine concentration in the total chlorine concentration.

15 In addition, the storage conditions when storing the water treatment agent of the second embodiment of the present technology after production thereof are not particularly limited, and storage at ordinary temperature or storage in a dark place at ordinary temperature is preferable, and temperature control at about 4 to 40°C is more preferable.
20 [0143] In addition, the water treatment agent of the second embodiment obtained by the production method of the second embodiment of the present technology can be marketed at an ordinary temperature of about 4 to 40°C and can suppress decrease in the concentration of the active component even if stored at ordinary temperature over a long period of
25 time (for example, for about 3 months after production). In addition, the water treatment agent of the second embodiment of the present technology can prevent the generation of a concentrated bromide solution

during mixing in the production step, and this can suppress the generation of hypochlorous acid in the water treatment agent of the second embodiment obtained to reduce decrease in the active component concentration, and as described above, a product stable in quality can be
5 provided.

[0144] The water treatment agent obtained by the production method of the second embodiment of the present technology has a higher total chlorine concentration after production and a free chlorine concentration that is as low as or less than that of the water treatment agent of Patent
10 Literature 2 or the water treatment agent of Patent Literature 3, and can exhibit the effect of interest better and is also superior in the quality stability of the agent.

[0145] In the present technology, the quality stability of an agent means that when the agent is stored for a certain period of time, the active
15 component in the agent is unlikely to be decomposed and the active component concentration is maintained within a certain range. More specifically, it is preferred that hypochlorous acid be unlikely to be generated in the agent and that decrease in the active component concentration be small.

[0146] In the water treatment agent of the second embodiment of the present technology, it is preferable to adjust the molar ratio of the chloramine compound to the bromide salt, and when the chloramine compound is 1, the molar ratio of the chloramine compound to the bromide salt is preferably 1:0.05 to 3.0, more preferably 1:0.1 to 1.5,
25 further preferably 1:0.1 to 1.0, and more further preferably 1:0.2 to 1.0. In the method of producing a water treatment agent according to the

second embodiment of the present technology, adjustment may be appropriately made to provide the above molar ratio.

[0147] The water treatment agent of the second embodiment of the present technology is excellent in the quality stability of the agent, and
5 can exhibit the effect of hypochlorous acid well, based on the alkali agent, the haloamine compound (preferably chloramine compound), and the bromide salt in the agent when added to a water system. Then, the water treatment agent of the second embodiment of the present technology can gradually generate hypobromous acid over time in the
10 water system, and thus can maintain the effect of hypobromous acid in the water system over a longer period of time more sustainably.

[0148] As another aspect of the water treatment agent of the second embodiment of the present technology, the water treatment agent can also be used as a sustained-release water treatment agent although the
15 water treatment agent is a one-component agent. Rapid release of hypobromous acid in the water system is likely to lead to corrosion or deterioration in the water system, but the water treatment agent of the second embodiment of the present technology can control the generation rate of hypobromous acid to be slow, and thus corrosion or deterioration
20 in the water system can be reduced, and also an effect (for example, microbial removal action) caused by hypobromous acid can be obtained over a long period of time sustainably. Because of this, it is more beneficial to apply the water treatment agent of the second embodiment of the present technology to, for example, an open circulation type
25 apparatus having a cooling water system, a heat storage water system, a dust collecting water system, a scrubber water system, or the like.

[0149] <3-2-3. Optional component of second embodiment of the present technology>

Somewhere in the production step of the water treatment agent of the second embodiment of the present technology, any optional agent as
5 an optional component can be mixed in a range that does not impair the effect of the present technology.

Examples of the optional agent include, but are not limited to, an anticorrosive agent (corrosion inhibitor), a scale preventive agent, a slime control agent, a solvent or dispersion medium such as water, a dispersant
10 enzyme, a microbicide, and a defoaming agent, and various agents that can be generally used for water treatment may be used. One or two or more selected from the group consisting of these can be used. As the optional agent, an agent described in the first embodiment can be appropriately adopted.

15 [0150] <Anticorrosive agent (corrosion inhibitor)>

The anticorrosive agent (corrosion inhibitor) is not particularly limited, and is preferably an anticorrosive agent for a cooling water system. For example, a polymer such as a carboxyl group polymer; and an azole such as benzotriazole or tolyltriazole are preferable.

20 [0151] The type of the carboxyl group polymer is not particularly limited, and examples thereof include a water-soluble homopolymer and/or copolymer having a carboxyl group, and further specifically, include a maleic acid-based polymer and a (meth)acrylic acid-based polymer. The "polymer" is meant to include a monopolymer and a
25 copolymer.

[0152] More specifically, examples of the carboxyl group polymer include a homomaleic acid polymer, a homo (meth)acrylic acid polymer, a

copolymer of a maleic acid or (meth)acrylic acid monomer and an unsaturated monomer copolymerizable therewith, and one selected from the group consisting of these can be used or two or more can be used in combination.

- 5 [0153] The carboxyl group polymer in the second embodiment of the present technology preferably contains a maleic acid-based polymer and/or a (meth)acrylic acid-based polymer. The content proportion (content) of the maleic acid-based polymer and/or the (meth)acrylic acid-based polymer in the carboxyl group polymer is preferably 50% by mass
10 or more, more preferably 80% by mass or more, and further preferably 90% by mass or more, more preferably 95% by mass or more, and further preferably 99% by mass or more, and the higher the content proportion in the carboxyl group polymer is, the easier it is to obtain the expected effect of the present technology.
- 15 [0154] In addition, examples of the unsaturated monomer copolymerizable with maleic acid or a (meth)acrylic monomer include 2-acrylamide-2-methylpropanesulfonic acid, 2-hydroxy-3-allyloxy-1-propanesulfonic acid, styrenesulfonic acid, vinylsulfonic acid, acrylamide, ethylene, propylene, isopropylene, butylene, isobutylene, hexene, 2-
20 ethylhexene, pentene, isopentene, octene, isooctene, vinyl alcohol, vinyl methyl ether, vinyl ethyl ether, and salts thereof.

Examples include one or two or more polymers selected from the group consisting of a homopolymer, a copolymer, obtained using one or two or more monomers selected from the monomers described above, and
25 copolymer(s) of the monomer(s) and isobutylene, and the like.

[0155] When an agent effect such as anticorrosion action is expected, the carboxyl group polymer has a weight average molecular weight

preferably on the order of 10^3 to 10^4 and more specifically preferably in the range of 200 to 50,000, more preferably in the range of 500 to 30,000, further preferably in the range of 800 to 30,000, and more preferably in the range of 1,000 to 20,000.

5 [0156] As the carboxyl group polymer, the carboxyl group polymer used in the first embodiment of the present technology and the amount used described above can be adopted. Further, in the second embodiment, what is obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing
10 agent is preferably a mixture containing a chloramine compound and the bromide salt, and it is more preferable to provide a water treatment agent or a water treatment agent kit that uses components (a) to (c) of the first embodiment by mixing the mixture and the carboxyl group polymer. Thereby, in addition to the effect of the second embodiment of the present
15 technology, as shown in the first embodiment of the present technology, it is also possible to provide a one-component water treatment technology that can also better exhibit an agent effect of another compound well.

[0157] The <Method of measuring weight average molecular weight of water-soluble polymer> in the second embodiment can be performed in
20 the same manner as the <Method of measuring weight average molecular weight of water-soluble polymer> described in the first embodiment described above.

[0158] <Scale preventive agent>

The scale preventive agent used in the second embodiment of the
25 present technology is not particularly limited, and the "scale preventive agent" used in the first embodiment of the present technology described above can be adopted.

[0159] The content of the anticorrosive agent and/or the scale preventive agent in the water treatment agent of the second embodiment of the present technology is not particularly limited, and is preferably 0.5 to 30% by mass and further preferably 1 to 20% by mass.

- 5 [0160] <3-3. Method of using water treatment agent of second embodiment of the present technology, and water treatment method using the water treatment agent>

As described above, the water treatment agent of the second embodiment of the present technology can be used as at least any of, for
10 example, one for slime control, one for anticorrosion, or one for scale prevention in expectation of an effect of hypobromous acid (for example, microbial removal action or slime control action).

[0161] The second embodiment of the present technology can provide use of or a method of using the water treatment agent of the second
15 embodiment of the present technology, and examples of the purpose of use thereof include water treatment in a water system, a sterilization method in a water system, a slime control method in a water system, an anticorrosion method in a water system, or a membrane scale prevention method in a water system.

20 In addition, the second embodiment of the present technology can also provide a water treatment method, a sterilization method, a slime control method, an anticorrosion method, or a scale prevention method involving adding the water treatment agent of the second embodiment of the present technology to a water system. Any configuration
25 overlapping with the configuration described for the water treatment agent of the present technology described above will be omitted as appropriate.

[0162] From the viewpoint of stability over time, the pH of the water system in the method of the second embodiment of the present technology is in the alkaline region, and is more preferably 7 to 10 and further preferably 8 to 9. In addition, the water temperature of the water system is not particularly limited, and is usually about 4 to 40°C.

[0163] The amount of the water treatment agent of the second embodiment of the present technology added to the water system is not particularly limited and is appropriately adjusted according to the various water systems to be treated, and usually, the water treatment agent is preferably continuously added or intermittently added at a concentration of 1 to 1000 mg/L to each water system to be treated.

[0164] In the second embodiment of the present technology, the timing of addition of the agent or each component in the water system is not particularly limited, and it may be added at the same time or separately. And/or, the place where the agent or each component is added in the water system is not particularly limited, and it may be added to the same place or a different place.

[0165] For example, for the intended use of slime control or scale prevention for the membrane, it is preferable to add the agent before membrane treatment. In addition, for slime control, sterilization, and anticorrosion for a pipe within a water system, the effect of the present technology can be obtained even at any time and any place in the water system.

The target of the second embodiment of the present technology is preferably a cooling water system, and more preferably the cooling water system is a cooling water system including a metal or a metal pipe of a cooling tank, a cooling tower, a heat exchanger, or the like.

[0166] In the second embodiment of the present technology, it may be used as a water treatment agent kit having the water treatment agent of the second embodiment of the present technology and an optional component separately.

5 For example, it is possible to provide, for example, a water treatment agent kit having a mixture containing (a) a chloramine compound and (b) a bromide salt obtained by the method of producing a water treatment agent according to the second embodiment, the mixture being housed in one container A and (c) a carboxyl group polymer having
10 a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer, the carboxyl group polymer being housed in one container B, wherein when these are mixed, the carboxyl group polymer has an amount of 1 to 18% by mass and a pH of 10 or more.

 In the case of the water treatment agent kit, the components may
15 be housed in their respective separate containers, or a two-agent mixed component and one component may be housed in their respective separate containers. In addition, an optional component may be appropriately included in each container. The use of or method of using the water treatment agent kit can be performed in the same manner as
20 the use of or method of using the water treatment agent described above.

[0167] The present technology can also adopt the following configurations.

- [1] A water treatment agent comprising the following components (a) to (c) and having a pH of 10 or more:
25 (a) a chloramine compound,
(b) a bromide salt, and

(c) 1 to 18% by mass of a carboxyl group polymer having a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.

- [2] The water treatment agent according to above [1], wherein a molar ratio of the chloramine compound to the bromide salt is 1:0.1 to 1.0.
- 5 • [3] The water treatment agent according to above [1] or [2], wherein the water treatment agent is at least any of one for slime control, one for anticorrosion, or one for scale prevention.
- [4] The water treatment agent according to any of above [1] to [3], wherein the water treatment agent uses what is obtained by mixing of a
10 mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.
- [5] The water treatment agent according to any of above [1] to [4], wherein the water treatment agent has a total chlorine detection rate after production of 95% or more and a free chlorine content rate in a total
15 chlorine concentration of 0.05% (as Cl₂) or less.
- [6] The water treatment agent according to any of above [1] to [5], wherein the carboxyl group polymer contains a maleic acid-based polymer and/or a (meth)acrylic acid-based polymer, and preferably contains 50% by mass or more of the same in the carboxyl group polymer.
- 20 • [7] The water treatment agent according to any of above [1] to [6], wherein a pH of the water treatment agent is 13 or more.
- [8] The water treatment agent according to any of above [1] to [7], wherein the bromide salt is one or more selected from an alkali metal bromide salt, ammonium bromide salt, an amine hydrobromide salt, and
25 an amine bromide salt.
- [9] A water treatment method, a sterilization method, a slime control method, an anticorrosion method, or a scale prevention method, wherein

the water treatment agent according to any of above [1] to [8] is added to a water system.

- [10] The method according to above [9], wherein the water treatment agent is added to the water system such that a carboxyl group concentration in the water system is 1 to 100 mg/L.
 - [11] A water treatment method, a sterilization method, a slime control method, an anticorrosion method, or a scale prevention method comprising adding the following components (a) to (c) to a water system at the same time or different times and/or at the same place or different places:
 - (a) a chloramine compound,
 - (b) a bromide salt, and
 - (c) 1 to 18% by mass of a carboxyl group polymer having a carboxyl group content rate of 0.8 g-COOH/g-polymer or less in the polymer.
 - [12] The method according to any of above [10] to [12], wherein the component (a) chloramine compound to the component (b) bromide salt are added in such a way as to have a molar ratio of 1:0.1 to 1.0, and/or the component (c) is added such that a concentration of a carboxyl group in the water system is 5 to 50 mg/L.
 - [13] The method according to any of above [9] to [12], wherein the water system is a cooling water system, and preferably the cooling water system is a cooling water system including a metal or a metal pipe of a cooling tank, a cooling tower, a heat exchanger, or the like.
- [0168] The present technology can also adopt the following configurations.
- [14] A method of producing a water treatment agent, comprising mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent,

and a bromide salt, and of an oxidizing agent. Preferably, an oxidizing agent is added to the mixed solution and mixed.

- [15] The method of producing a water treatment agent according to above [14], wherein the stabilizing agent is a sulfamic acid compound.

5 Preferably, the sulfamic acid compound is the compound represented by the general formula (1) or a salt thereof. Of these, sulfamic acid or a salt thereof is more preferable.

- [16] The method of producing a water treatment agent according to above [14] or [15], wherein the oxidizing agent is a chlorine-based

10 oxidizing agent. The chlorine-based oxidizing agent is preferably one or two or more selected from a hypochlorite, chlorine dioxide, and chlorine gas.

- [17] The method of producing a water treatment agent according to any of above [14] to [16], wherein a pH of the mixed solution is 12 or more

15 (preferably 13 or more). When the oxidizing agent is mixed, the pH of the mixed solution is preferably adjusted.

- [18] The method of producing a water treatment agent according to any of above [14] to [17], wherein the mixed solution is obtained by mixing a powdered bromide salt as the bromide salt.

20 • [19] The method of producing a water treatment agent according to any of above [14] to [18], wherein a carboxyl group polymer is further mixed in such a way as to provide 1 to 18% by mass, and a carboxyl group content rate in the carboxyl group polymer is 0.8 g-COOH/g-polymer or less. It is preferable to further mix the mixed solution and the carboxyl
25 group polymer.

- [20] The method of producing a water treatment agent according to any of above [14] to [19], wherein the mixed solution of the alkali agent, the

stabilizing agent, and the bromide salt is obtained by mixing the alkali agent into a solution and then mixing the stabilizing agent and/or the bromide salt at the same time or separately.

- [21] The method of producing a water treatment agent according to any of above [14] to [20], wherein a molar ratio of the chloramine compound to the bromide salt in the water treatment agent is adjusted to be 1:0.05 to 3.0 when the chloramine compound is 1.

[0169] • [22] A water treatment agent obtained by the method of producing a water treatment agent according to any of above [14] to [21].

- 10 Preferably, the water treatment agent contains an alkali agent, a haloamine compound (preferably a chloramine compound), and a bromide salt.

- [23] A water treatment agent comprising an alkali agent, a chloramine compound, and a bromide salt, wherein

- 15 a total chlorine detection rate after production is 95% or more, and a free chlorine content rate in a total chlorine concentration is 0.05% (as Cl_2) or less. Further, the total chlorine concentration after production is preferably 4.1% (as Cl_2) or more.

- [24] The water treatment agent according to above [22] or [23], wherein

- 20 the water treatment agent is obtained by mixing of a mixed solution obtained by mixing an alkali agent, a stabilizing agent, and a bromide salt, and of an oxidizing agent.

- [25] The water treatment agent according to any of above [22] to [24], wherein a carboxyl group polymer is further mixed in such a way as to

- 25 provide 1 to 18% by mass, and a carboxyl group content rate in the carboxyl group polymer is 0.8 g-COOH/g-polymer or less.

The carboxyl group polymer preferably contains a maleic acid-based polymer and/or a (meth)acrylic acid-based polymer, and more preferably contains 50% by mass or more of the same in the carboxyl group polymer.

- [26] The water treatment agent according to any of above [21] to [24],
5 wherein a pH of the water treatment agent is 13 or more.
 - [27] The water treatment agent according to any of above [21] to [26],
wherein the water treatment agent is a sustained-release preparation of hypobromous acid.
 - [28] The water treatment agent according to any of above [21] to [27],
10 wherein the water treatment agent further comprises an antiseptic agent and/or a scale preventive agent. Preferably, the water treatment agent contains 0.5 to 30% by mass of an antiseptic agent and/or a scale preventive agent.
- [0170] • [29] A water treatment method, a sterilization method, a slime
15 control method, an anticorrosion method, or a scale prevention method, comprising adding the water treatment agent obtained by the method of producing a water treatment agent according to any of above [14] to [21] or the water treatment agent according to any of above [22] to [28] to a water system.

- 20 It is preferably applied to a water treatment apparatus. It is applied to, for example, an open circulation type apparatus having a cooling water system, a heat storage water system, a dust collecting water system, a scrubber water system, or the like.

- Preferably, the water treatment agent is continuously added or
25 intermittently added at a concentration of 1 to 1000 mg/L to each water system to be treated.

[0171] • [30] A water treatment apparatus or a water treatment system comprising an apparatus or a system for adding a water treatment agent or each component used in the water treatment agent, wherein

the water treatment agent is the water treatment agent according
5 to any of above [1] to [14] or the water treatment agent according to any of above [23] to [28].

The water treatment apparatus or water treatment system may further include an apparatus or a system for storage and/or an apparatus or a pipe, or a system for mixing. The water treatment apparatus or
10 water treatment system may further include a control apparatus or a control system for controlling the method according to any of above [9] to [13] and/or the method according to above [29].

Each component used in the water treatment agent according to any of above [1] to [14] and each component used in the water treatment
15 agent according to any of above [22] to [28] may appropriately be blended and used. The effect of hypobromous acid may be exhibited by mixing each component to make a water treatment agent and adding the same to the water system. In addition, each component may be added to the
20 water system at the same time or sequentially, and each component added may be mixed in the water system to exhibit the effect of hypobromous acid.

Examples

[0172] The embodiments of the present technology will be described
25 with reference to the following Test Examples, Examples, Comparative Examples, and the like. The scope of the present technology is not limited to the Test Examples, the Examples, and the like.

[0173] <Test Examples 1 to 28 (first embodiment)>

[Test Examples 1 to 4: Combination of each component: samples 1 to 4]

Each of samples 1 to 4 was added to open circulation type cooling water (pH 8 to 9) in such a way as to provide 0.8 g of sample (water
5 treatment agent)/L of water, and change over time in the total oxidizing agent concentration in the water system is shown in Fig. 1.

The water treatment agent (×) of sample 1 in Test Example 1 contains a chloramine compound concentration of 9%.

The water treatment agent (Δ) of sample 2 in Test Example 2
10 contains a chloramine compound concentration of 9% and a bromide concentration of 3.9%.

The water treatment agent (□) of sample 3 in Test Example 3 contains a chloramine compound concentration of 9% and a carboxyl group polymer concentration of 1.6%.

15 The water treatment agent (◇) of sample 4 in Test Example 4 contains a chloramine compound concentration of 9%, a carboxyl group polymer concentration of 1.6%, and a bromide concentration of 3.9%, and has a pH of 13.

[0174] The chloramine compound used in Test Examples 1 to 28 was
20 obtained by reacting hypochlorous acid and sulfamic acid ($\text{HN}_2\text{SO}_2\text{OH}$) and adjusted such that the Cl_2/N molar ratio was 0.1 to 1.

In addition, the bromide salt used in Test Examples 1 to 28 is potassium bromide.

[0175] In addition, the carboxyl group polymer used in Test Examples 1
25 to 4 is a maleic acid polymer (99% by mass or more), the carboxyl group content rate in the polymer is 0.77 g-COOH/g-polymer, and the weight average molecular weight of the carboxyl group polymer is 3,900.

The carboxyl group content rate in the carboxyl group polymer was measured by the <Method of measuring carboxyl group content rate (g-COOH/g-polymer)> described above.

5 The weight average molecular weight of the carboxyl group polymer was measured by the <Method of measuring weight average molecular weight of water-soluble polymer> described above.

[0176] Each measurement method used in each [Test Example] is shown below.

<Total oxidizing agent concentration>: The total concentration of
10 chloramine, hypochlorous acid, and hypobromous acid was measured using a DPD total reagent. The total oxidizing agent concentration is converted in terms of chlorine and expressed in mg/L, as Cl₂.

<Hypobromous acid>: After reacting free chlorine with glycine, the remaining hypobromous acid was measured using a DPD-free reagent.
15 The hypobromous acid concentration is converted in terms of chlorine and expressed in mg/L, as Cl₂.

The DPD method used in the present technology is performed according to the DPD method that uses JIS K 0400-33-10:1999 N,N-diethyl-1,4-phenylenediamine.

20 [0177] Fig. 1 shows change over time in the total oxidizing agent concentration when the carboxyl group polymer and/or the bromide are/is caused to coexist, with the concentration when only the chloramine compound is added as 100%.

No difference in the residual rate was found when the carboxyl
25 group polymer and the bromide were added to the chloramine compound respectively alone, whereas the residual rate decreased by 10% or more

when both the carboxyl group polymer and the bromide were added to the chloramine compound.

The residual rate was remarkably decreased only when the chloramine compound, the bromide, and the carboxyl group polymer
5 coexisted, and thus it was considered that hypobromous acid generated in the water system reacted with the carboxyl group polymer and was decomposed.

[0178] As described above, in the water treatment agent of sample 4, a pharmacological effect of the carboxyl group polymer can be expected.

10 However, although sample 4 is designed to utilize hypobromous acid, which is stronger than hypochlorous acid, sample 4 is not very good in the stability over time of hypobromous acid in the water system, and thus an effect (for example, microbial removal effect) of hypobromous acid was also considered to be lack of sustainability. Because of this, it was
15 considered that, using sample 4, it is difficult to provide a one-component water treatment agent that can exhibit an effect of hypobromous acid well when added to a water system and also exhibit an agent effect of another compound well.

[0179] [Test Examples 5 to 16: Carboxyl group content rate of carboxyl
20 group polymer]

As each water treatment agent used in Test Examples 5 to 16, one prepared based on one containing a chloramine compound concentration of 9%, a carboxyl group polymer concentration of 1.6%, and a bromide concentration of 3.9%, and having a pH of 13 was used.

25 The carboxyl group polymer used in each water treatment agent used in Test Examples 5 to 16 was a maleic acid polymer, and one having

a weight average molecular weight in the range of 1,000 to 16,000 was used.

[0180] At this time, as the carboxyl group polymer of each water treatment agent, one having a carboxyl group content rate (g-COOH/g-polymer) in the carboxyl group polymer as shown in Table 1 and Table 2 was used.

Specifically, when the carboxyl group content rate in the carboxyl group polymer was measured in each water treatment agent of Test Examples 5 to 16, results were as follows: Test Examples 5 and 11: 0.63 g-COOH/g-polymer, Test Examples 6 and 12: 0.43 g-COOH/g-polymer, Test Examples 7 and 13: 0.49 g-COOH/g-polymer, Test Examples 8 and 14: 0.52 g-COOH/g-polymer, Test Examples 9 and 15: 0.71 g-COOH/g-polymer, and Test Examples 10 and 16: 0.77 g-COOH/g-polymer.

[0181] Further, each water treatment agent was prepared such that the carboxyl group polymer concentration in the water treatment agent was 5 mg-polymer/L when added to 1 L of water, and each was used in Test Examples 5 to 10.

In addition, each water treatment agent was prepared such that the carboxyl group polymer concentration in the water treatment agent was 30 mg-polymer/L when added to 1 L of water, and each was used in Test Examples 11 to 16.

The molar ratio of the chloramine compound to the bromide salt of each water treatment agent used in Test Examples 5 to 16 was 1:0.2 to 1.0 when the chloramine compound was 1.

[0182] In Test Examples 5 to 10, each water treatment agent was added to open circulation type cooling water (pH 8 to 9) in such a way as to have a carboxyl group polymer concentration of 5 mg-polymer/L, and after 48

hours, the hypobromous acid concentration (mg/L as CL_2) in the water system was measured. Results thereof are shown in Fig. 2 and Table 1.

[0183] In Test Examples 11 to 16, each water treatment agent was added to open circulation type cooling water (pH 8 to 9) in such a way as
5 to have a carboxyl group polymer concentration of 30 mg-polymer/L, and after 48 hours, the hypobromous acid concentration (mg/L as CL_2) in the water system was measured. Results thereof are shown in Fig. 3 and Table 2.

[0184]

Table 1

	Carboxyl group content rate in polymer (g- COOH/g-polymer)	Total oxidizing agent(%)	Hypobromous acid(%)
Test Example 5	0.62845	101.04	96.11
Test Example 6	0.42597	101.56	97.78
Test Example 7	0.49002	100.00	103.33
Test Example 8	0.51983	98.44	102.78
Test Example 9	0.70603	99.48	101.67
Test Example 10	0.77486	100.00	103.89

[0185]

Table 2

	Carboxyl group content rate in polymer (g- COOH/g-polymer)	Total oxidizing agent(%)	Hypobromous acid(%)
Test Example 11	0.62845	95.36	98.48
Test Example 12	0.42597	94.85	103.55
Test Example 13	0.49002	92.78	100.51
Test Example 14	0.51983	93.30	96.45
Test Example 15	0.70603	93.81	100.30
Test Example 16	0.77586	86.60	79.19

[0186] [Test Examples 17 to 27: Carboxyl group polymer concentration

5 in water system]

Based on the water treatment agent used in Test Example 5, the carboxyl group polymer concentration in the water system was changed as shown in Table 3 to obtain each water treatment agent used in Test Examples 17 to 29.

10 In Test Examples 17 to 27, each water treatment agent was added to open circulation type cooling water (pH 8 to 9) in such a way as to have a carboxyl group polymer concentration (mg-polymer/L) in the water system as shown in Table 3 below. The hypobromous acid concentration (mg/L as CL_2) in the water system was measured 48 hours after the

15 addition of each water treatment agent. Results thereof are shown in Fig. 4 and Table 3.

[0187]

Table 3

	Carboxyl group polymer concentration in polymer in water system (mg-polymer/L)	Hypobromous acid concentration(%)
Test Example 17	3.1	96.1
Test Example 18	1.8	97.8
Test Example 19	1.9	103.3
Test Example 20	2.6	102.8
Test Example 21	3.5	101.7
Test Example 22	3.9	103.9
Test Example 23	18.8	89.3
Test Example 24	10.7	103.9
Test Example 25	11.1	96.1
Test Example 26	15.5	97.1
Test Example 27	21.1	100.0

[0188] <Summary>

The results of Test Examples 5 to 16 are shown in Fig. 2 and Fig. 3 and Table 1 and Table 2. The results of Test Examples 17 to 27 are shown in Fig. 4 and Table 3.

The carboxyl group polymer used in the water treatment agent can maintain the hypobromous acid concentration in the water system to which the water treatment agent was added at about 80% when the carboxyl group content rate in the polymer is 0.77. Further, from the viewpoint of being able to set the hypobromous acid concentration in the water system to which the water treatment agent was added to 90% or more, it was better when the carboxyl group content rate in the polymer was more preferably 0.35 to 0.75.

In addition, when the concentration of the carboxyl group polymer in the water system in the case of adding the water treatment agent to the water system was 5 to 30 mg-polymer/L, the total oxidizing agent concentration (%) and the hypobromous acid concentration (%) in the water system were high and good.

- [0189] Further, the amount of the water treatment agent added to the water system is preferably 40 to 200 mg/L from the viewpoint of effect and cost. Further, as described above, considering that the concentration of the carboxyl group polymer in the water system when
- 5 the water treatment agent is added to the water system is preferably 5 to 30 mg-polymer/L, it is preferred to set the concentration of the carboxyl group polymer contained in the water treatment agent to 18% by mass or less (more preferably 15% by mass or less), and it is preferred to set the same to 1% by mass or more (more preferably 1.5% by mass or more) from
- 10 the viewpoint of cost, work efficiency, effect exhibition, and the like. This means that, for example, [polymer concentration in water system of 30 mg-polymer/L]/[amount of water treatment agent added to water system of 200 mg/L] = polymer content in water treatment agent of 0.15 mg-polymer/mg (that is, 15% by mass) can be determined.
- 15 [0190] In addition, even with the water treatment agent in which the maleic acid polymer used in the water treatment agent of Test Example 7 was replaced with an acrylic acid polymer (carboxyl group content rate in the polymer of 0.5 g-COOH/g-polymer; weight average molecular weight of 1,000 to 16,000), the same effect as that of the water treatment agent of
- 20 Test Example 7 was able to be obtained.
- [0191] In addition, the total oxidizing agent concentration of each water treatment agent of Test Examples 5 to 16 was 98% or more when stored at 20°C for 20 days and 90% or more when stored at 50°C for 20 days, in stationary storage in a constant temperature bath.
- 25 [0192] [Test Example 28: Sustained release properties and weight average molecular weight of carboxyl group polymer]

As shown in Table 4, the water treatment agent used in Test Example 5 was added to open circulation type cooling water (pH 8 to 9) in such a way as to have a carboxyl group polymer concentration of 0.2 g/L, and the hypobromous acid concentration (mg/L as CL_2) in the water system was measured over time.

[0193] In addition, the same test was performed by replacing the carboxyl group polymer having a weight average molecular weight of 3,900 used in the water treatment agent of Test Example 5 with each of ones having a weight average molecular weight of 800, 14,000, and 20,000, respectively. Even with these carboxyl group polymers having a weight average molecular weight on the order of 10^3 to 10^4 , almost the same hypobromous acid concentration as that with the carboxyl group polymer having a weight average molecular weight of 3,900 was able to be obtained. When a carboxyl group polymer having a weight average molecular weight of about 1,000 to 20,000 was used, a better hypobromous acid concentration (about 40 to 60%) was able to be obtained.

The carboxyl group content rate in the polymer was measured by the <Method of measuring carboxyl group content rate (g-COOH/g-polymer)> described above.

The weight average molecular weight of the carboxyl group polymer was measured by the <Method of measuring weight average molecular weight of water-soluble polymer> described above.

[0194] The water treatment agent of the first embodiment can be adjusted such that the hypobromous acid concentration 48 hours after the addition to the water system is preferably 0.25 to 1.5 mg/L as CL_2 and more preferably 0.5 to 1 mg/L as CL_2 .

[0195]

Table 4

Elapsed time (hr)	Hypobromous acid (mg/L as Cl ₂)
0	0
0.25	0
0.5	0.02
2	0.03
72	1.1
96	1.54

[0196] <Test Examples 29 to 31 (second embodiment)>

Each measurement method used in each [Test Example] is shown
5 below.

<Total oxidizing agent concentration>: The total concentration of
chloramine, hypochlorous acid, and hypobromous acid was measured
using a DPD total reagent. The total oxidizing agent concentration is
converted in terms of chlorine and expressed in mg/L, as Cl₂.

10 <Hypobromous acid>: After reacting free chlorine with glycine,
the remaining hypobromous acid was measured using a DPD-free reagent.
The hypobromous acid concentration is converted in terms of chlorine and
expressed in mg/L, as Cl₂.

The DPD method used in the present technology is performed
15 according to the DPD method that uses JIS K 0400-33-10:1999 N,N-
diethyl-1,4-phenylenediamine.

[0197] [Test Examples: Test Example 29 (Example 1), Test Example 30
(Comparative Example 1), and Test Example 31 (Comparative Example
2)]

20 In the present test, each component of Table 5 was blended into
water (about 10 to 20°C) in the mixing order shown in Table 5 to prepare
each one-component water treatment agent.

At this time, each component shown in Table 5 was blended in such a way as to provide 20% by mass (balance) of water, 10% by mass of sodium sulfamate, 5% by mass of sodium bromide, and a pH of 14 in the water treatment agent immediately after production (0 hours). Sodium hydroxide was used as the alkali agent, and powdered sodium bromide was used as sodium bromide. Sodium hypochlorite was used in such a way as to provide 1 mol of hypochlorous acid (free form) per 1.5 mol of sulfamic acid (free form).

In addition, in Test Example 29 (Example 1) and Test Examples 30 and 31 (Comparative Examples 1 and 2), the theoretical value of the total chlorine concentration (%) (as Cl_2) in a water treatment agent generated computationally when sodium sulfamate and sodium hypochlorite are mixed is 4.4%. Each "total chlorine detection rate (%)" of Test Example 29 (Example 1) and Test Examples 30 and 31 (Comparative Examples 1 and 2) shown in Table 2 and Fig. 5 was calculated from the "measured value (% as Cl_2) of total chlorine concentration in water treatment agent/theoretical value (% as Cl_2) of total chlorine concentration in water treatment agent" $\times 100$ (%).

[0198] About the method of producing water treatment agent of Test Example 29 (Example 1);

To 1.0 L of water, 500 g of sodium hydroxide was added and mixed to adjust the pH to 14 or more to obtain an alkali agent mixed aqueous solution.

To this alkali agent mixed aqueous solution, 400 g of sodium sulfamate and then 250 g of powdered sodium bromide were added and mixed to obtain a three-agent mixed aqueous solution.

To this three-agent mixed aqueous solution, 2000 g of sodium hypochlorite was added and mixed to obtain a water treatment agent. Adjustment was made such that sodium hypochlorite was added in such a way as to provide 1.5 mol of sulfamic acid (free form) per mol of
5 hypochlorous acid (free form).

As sodium sulfamate, one manufactured by Tokyo Chemical Industry Co., Ltd., as powdered sodium bromide, one manufactured by Tokyo Chemical Industry Co., Ltd., and as sodium hypochlorite, one manufactured by Nippon Light Metal Company, Ltd. were used.

10 The concentration of each component in the one-component water treatment agent is as described above.

In addition, the "free chlorine content rate (%) in total chlorine concentration" was calculated from the [free chlorine concentration (% as Cl_2) in water treatment agent/total chlorine concentration (% as Cl_2) in
15 water treatment agent] $\times$ 100 (%).

[0199] In addition, when preparing the three-agent mixed aqueous solution as the water treatment agent of Test Example 32 (Example 2), the order of addition of sodium sulfamate and powdered sodium bromide was changed. That is, powdered sodium bromide and then sodium
20 sulfamate were added to the alkali agent mixed aqueous solution and mixed to prepare a three-agent mixed aqueous solution. 4 hours after the production, the total chlorine concentration in the water treatment agent of Test Example 32 (Example 2) was 4.3 (% as Cl_2), and the free chlorine content rate in the total chlorine concentration was 0.04 (% as
25 Cl_2). Therefore, the water treatment agent of Test Example 32 (Example 2) had substantially the same quality stability as the quality stability of the water treatment agent of Test Example 29 (Example 1).

[0200] Each water treatment agent (Test Example 29 (Example 1) and Test Examples 30 and 31 (Comparative Examples 1 and 2)) was stored at an aqueous solution temperature of about 15 to 25°C for a certain period of time after production. The total chlorine concentration and the free chlorine in each water treatment agent were measured for each elapsed time (1, 2, 3, and 4 hr) after production, and results thereof are shown in Table 6.

[0201]

Table 5: Production process of each water treatment agent

Test Example 29 (Example 1)	Test Example 30 (Comparative Example 1)	Test Example 31 (Comparative Example 2)
Water ↓ Alkali agent ↓ Sodium sulfamate ↓ Sodium bromide ↓ Sodium hypochlorite	Water ↓ Alkali agent ↓ Sodium sulfamate ↓ Sodium hypochlorite ↓ Sodium bromide	Water ↓ Sodium sulfamate ↓ Sodium bromide ↓ Sodium hypochlorite ↓ Alkali agent

[0202]

Table 6: Total chlorine concentration and free chlorine content rate in total chlorine concentration in each water treatment agent

	Test Example 29 (Example 1)		Test Example 30 (Comparative Example 1)		Test Example 31 (Comparative Example 2)	
Elapsed time (hr)	Total chlorine concentration (% as Cl ₂)	Free chlorine content rate in total chlorine concentration (% as Cl ₂)	Total chlorine concentration (% as Cl ₂)	Free chlorine content rate in total chlorine concentration (% as Cl ₂)	Total chlorine concentration (% as Cl ₂)	Free chlorine content rate in total chlorine concentration (% as Cl ₂)
1	4.4	0.03	4.3	0.04	4.2	0.90
2	4.3	0.04	4.1	0.05	3.3	0.70
3	4.3	0.04	4.1	0.05	3.0	0.80
4	4.3	0.04	4.1	0.05	2.8	0.70

[0203]

Table 7: Total chlorine detection rate in each water treatment agent

	Test Example 29 (Example 1)	Test Example 30 (Comparative Example 1)	Test Example 31 (Comparative Example 2)
Elapsed time (hr)	Total chlorine detection rate (%)	Total chlorine detection rate (%)	Total chlorine detection rate (%)
1	100.0	97.7	95.5
2	97.7	93.2	75.0
3	97.7	93.2	68.2
4	97.7	93.2	63.6

The theoretical value of the total chlorine concentration was set to 4.4 (%) (as Cl₂).

- 5 [0204] As shown in Test Example 29 (Example 1) in Tables 5 to 7, by preparing a mixed solution obtained by mixing agents other than the bromide salt adding the bromide salt to the mixed solution and mixing these, a one-component water treatment agent containing the chloramine compound + a bromide ion can be obtained, and by such a production
- 10 procedure, a water treatment agent exhibiting an effect of hypobromous acid well when added to a water system while being excellent in the quality stability of the agent was able to be obtained.

- Specifically, in the water treatment agent of Test Example 29 (Example 1), 4 hours after the production, the total chlorine detection
- 15 rate (%) leveled off at about 98% and the total chlorine concentration (% as Cl₂) leveled off at 4.3%, and the free chlorine content rate in the total chlorine concentration also leveled off at 0.04%. It is considered that the active component in the water treatment agent is in a stable state because of such leveling off, and thus it is considered that this stable
- 20 state will last for several weeks or more.

[0205] On the other hand, in the water treatment agent of Test Example 31 (Comparative Example 2), the total chlorine concentration continues to decrease even 4 hours after the production, and it is considered that the total chlorine detection rate will be much less than
5 60% and the total chlorine concentration (% as Cl_2) will be much less than 2.8% thereafter. In addition, in the water treatment agent of Test Example 30 (Comparative Example 1), 4 hours after the production, the total chlorine detection rate leveled off at about 93% and the total chlorine concentration (% as Cl_2) leveled off at 4.1%, and the free chlorine
10 content rate in the total chlorine concentration was also in the state of leveling off at 0.05%.

[0206] One hour after the production and 4 hours after the production, the loss of the total chlorine detection rate of the water treatment agent of Test Example 29 (Example 1) was about 3%, whereas the total chlorine
15 detection rate of the water treatment agent of Test Example 30 (Comparative Example 1) was about 7%. When comparing the loss rate of the total chlorine concentration in the water treatment agent of Test Example 29 (Example 1) with the loss rate of the total chlorine concentration of the water treatment agent of Test Example 30
20 (Comparative Example 1), the water treatment agent of Test Example 29 (Example 1) was able to suppress the loss rate to less than half and maintain the state of being close to substantially 100% and thus can be deemed to be quite excellent in quality stability.

As described above, the water treatment agent of the second
25 embodiment of the present technology can maintain an active component high, and thus can be deemed to exhibit an effect of hypobromous acid

well when added to a water system, and to be excellent in the quality stability of the agent.

[0207] In addition, the total chlorine concentration (% as Cl_2) of the water treatment agent of Test Example 30 (Comparative Example 1) after 2 hours is 4.1% or less, whereas the chlorine concentration (% as Cl_2) of the water treatment agent of the second embodiment of the present technology is maintained at at least 4.2% or more even after 2 hours, and the water treatment agent obtained by the production method of the second embodiment of the present technology can be deemed to be a novel water treatment.

[0208] The water treatment agent of the second embodiment of the present technology produced by such a procedure is excellent in the quality stability of the agent and can suppress decrease in the active component very much, and thus can generate hypobromous acid at a high concentration when added to a water system. Therefore, the water treatment agent of the second embodiment of the present technology can generate hypobromous acid at a higher concentration when added to a water system than another water treatment agent, and that is, can exhibit an effect of hypobromous acid well. Therefore, the water treatment agent of the second embodiment of the present technology can exhibit an effect of hypobromous acid such as high microbicidal effect or high slime prevention effect more.

[0209] In addition, the water treatment agent of the second embodiment of the present technology did not develop such an action/effect by using a special apparatus or by including another agent, but was able to exhibit such an excellent effect by designing a mixing procedure of each component. That is, the production method of the second embodiment of

the present technology derived as described above and the water treatment agent obtained by the production method have been able to reduce the cost, improve the work efficiency, and enhance the quality stability, and from this viewpoint as well, it can be deemed that the
5 second embodiment of the present technology has found an unpredictable configuration and an unpredictable effect due thereto.

CLAIMS

[Claim 1]

5 A method of producing a water treatment agent, comprising mixing
of a mixed solution obtained by mixing an alkali agent, a stabilizing agent,
and a bromide salt, and of a halogen-based oxidizing agent, and preparing
the water treatment agent containing a chloramine compound and 1% or
more of the bromide salt,

wherein

10 the mixed solution is prepared by adding and mixing the stabilizing
agent and the bromide salt into an aqueous solution adjusted to pH 13 or
more with the alkali agent before adding the halogen-based oxidizing
agent,

15 1.2 to 3 mol of the stabilizing agent is blended per mol of the
halogen-based oxidizing agent,

the stabilizing agent is a sulfamic acid compound,

the halogen-based oxidizing agent is hypochlorous acid or a salt
thereof, and

a pH of the water treatment agent is 13 or more.

20 [Claim 2]

The method of producing a water treatment agent according to
claim 1, wherein the mixed solution is obtained by adding and mixing a
powdered bromide salt as the bromide salt.

[Claim 3]

25 The method of producing a water treatment agent according to any
of claims 1 or 2, wherein a carboxyl group polymer is further mixed in

such a way as to provide 1 to 18% by mass, and a carboxyl group content rate in the carboxyl group polymer is 0.8 g-COOH/g-polymer or less.

WATER TREATMENT AGENT

ABSTRACT

To provide a water treatment agent which exhibits an effect of
5 hypobromous acid well when added to a water system. A water
treatment agent comprising the following components (a) to (c): (a) a
chloramine compound, (b) a bromide salt, and (c) 1 to 18% by mass of a
carboxyl group polymer having a carboxyl group content rate of 0.8 g-
COOH/g-polymer or less in the polymer, and having a pH of 10 or more,
10 and/or a water treatment agent comprising an alkali agent, a chloramine
compound, and a bromide salt, and having a total chlorine detection rate
after production of 95% or more and having a free chlorine content rate in
a total chlorine concentration of 0.05% (as Cl₂) or less. The molar ratio
of the chloramine compound to the bromide salt is preferably 1:0.1 to 1.0.

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No figure