

DESCRIPTION

Title of invention: METHOD FOR PREVENTING ADHESION OF
MARINE ORGANISMS, ADHESION PREVENTIVE AGENT, AND ADHESION
5 PREVENTIVE KIT

TECHNICAL FIELD

[0001]

10 The present invention relates to a method for
preventing adhesion of marine organisms and the like, an
agent for preventing adhesion of marine organisms and the
like, and a kit for preventing adhesion of marine organisms
and the like.

15 BACKGROUND ART

[0002]

Plants that use seawater as cooling water, such as
power plants, steelworks, and petrochemical plants, are
often built facing inland seas or bays to avoid waves.
20 Seawater taken from inland seas or bays contains marine
organisms living in seawater, such as blue mussels,
barnacles, bryozoans, and hydrozoans, slime and the like,
and they adhere to seawater intake channels, pipes, conduit
channels, heat exchangers, condenser tubes, and other
25 waterways, causing various troubles. For example, attached
marine organisms and the like may grow to block conduit
channels such as heat exchanger tubes, thereby blocking the
passage of seawater, and also create turbulence to cause
erosion corrosion and other troubles. When attached marine
30 organisms and the like are stripped off by water pressure,
flow velocity, or the like, they cause blockages in tubes
and strainers of heat exchangers, which inhibit seawater
passage to cause a decrease in the original functions of
the heat exchangers.

35 A season of adhesion and growth of the marine

organisms in the seas around Japan is normally considered to be from April to October, but they can grow even in winter due to high seawater temperatures, influx of exotic species, and other factors, causing the troubles described
5 above.

[0003]

In order to prevent adhesion (attachment) of the above marine organism species, a chlorine generator (also called "a chlorine agent") such as sodium hypochlorite,
10 electrolytic chlorine, or chlorine gas, hydrogen peroxide, or a hydrogen peroxide generator (also called "a hydrogen peroxide agent") has been conventionally added (see Patent Literature 1 and Patent Literature 2).

[0004]

15 For example, Patent Literature 3 discloses an art relating to an agent for controlling aquatic adhesive organisms which contains, as an active ingredient, chlorine dioxide or a chlorine dioxide generator. Patent Document 4 discloses an art relating to a method for preventing or
20 controlling adhesion of organisms adhering to waterways. The method includes injecting a chlorine dioxide aqueous solution continuously or a relatively high concentration chlorine dioxide aqueous solution intermittently to waterways that pass freshwater or seawater provided in
25 facilities where freshwater or seawater is used.

Chlorine dioxide used here is highly bactericidal and does not form compounds such as trihalomethanes, and therefore advantageously has a low environmental impact.

30 However, chlorine dioxide is an extremely unstable chemical substance, and therefore cannot maintain its effect of preventing adhesion of marine organisms for a long time.

The present applicant has also proposed a method for preventing adhesion of marine organisms which combines
35 chlorine dioxide and hydrogen peroxide, and an adhesion

preventive agent for use in the method (Patent Literature 5).

[0005]

Patent Literature 6 or the like discloses a
5 stabilized chlorine agent such as sodium chlorosulfamate
and a stabilized bromine agent such as sodium
bromosulfamate as slime controlling agents that can prevent
biofouling disorders without causing degradation of RO
membranes used in seawater desalination equipment and the
10 like.

[0006]

Quaternary ammonium compounds and higher aliphatic
amine compounds have also been proposed as highly safe
agents for preventing attachment of marine attaching
15 organisms (Patent Literature 7).

[0007]

Also proposed with an aim of efficiently suppressing
frothing in systems such as seawater cooling water systems
in which chlorine generators are added to prevent adhesion
20 of marine organisms is a method of inhibiting frothing in a
seawater cooling water system, including adding a specific
higher aliphatic tertiary amine to a seawater cooling water
system in which frothing has occurred after addition of a
chlorine generator (Patent Literature 8). However, this
25 document is intended to provide a method of suppressing
frothing in seawater cooling water systems which can
efficiently suppress frothing, and is not to be implemented
in seawater cooling water systems where frothing does not
occur. Moreover, addition of a higher aliphatic tertiary
30 amine in the method is not intended to prevent adhesion of
marine organisms.

CITATION LIST

- Patent Literature

35 [0008]

Patent Literature 1: JP H11-37666 A
Patent Literature 2: JP S61-2439 B
Patent Literature 3: JP H01-275504 A
Patent Literature 4: JP H06-153759 A
5 Patent Literature 5: JP 5879596 B
Patent Literature 6: JP 2006-263510 A
Patent Literature 7: JP 2634958 B
Patent Literature 8: WO 2008/041400

10 SUMMARY OF INVENTION

- Technical problem
[0009]

15 In preventing adhesion of marine organisms, there is a movement to avoid use of halogen-type chemicals such as chlorine agents and bromine agents in consideration of an influence on the environment. Under the current circumstances, however, use of chlorine agents and bromine agents is sometimes unavoidable because of the use of old plant equipment.

20 Under these circumstances, it is desired to develop a method for preventing adhesion of marine organisms and the like which can exhibit an excellent effect of preventing adhesion of marine organisms and slime while using smaller amounts of halogen-type chemicals such as chlorine agents
25 and bromine agents.

Chemicals containing quaternary ammonium salts and higher aliphatic amine compounds are relatively expensive, and therefore addition of such chemicals at high concentrations or in large amounts is not economically
30 desirable. Development of an inexpensive method is awaited.

[0010]

The present invention aims to provide a method for preventing adhesion of marine organisms and the like which
35 uses smaller amounts of a halogen-type chemical such as a

chlorine agent and a bromine agent and chlorine dioxide, as well as a smaller amount of a higher aliphatic tertiary amine, while maintaining the effects of them for a long time, and can prevent adhesion of a wide range of marine organism species and slime, and also aims to provide an agent and kit for preventing adhesion for use in the method.

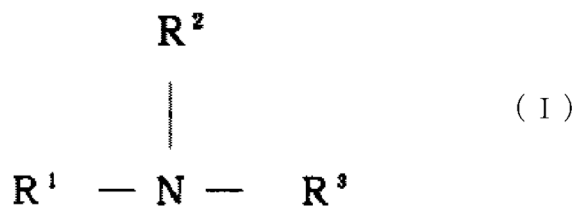
- Solution to problem

10 [0011]

The present inventors found out that combination use of a first chemical containing a higher aliphatic tertiary amine and a second chemical containing at least one selected from the group consisting of a chlorine agent, a bromine agent, and chlorine dioxide can effectively prevent adhesion of a wide range of marine organism species including mussels (e.g., blue mussels) and barnacles and adhesion of slime, and the effect of preventing adhesion of marine organisms and slime is sufficient even when the addition amounts of the chemicals are reduced, compared to the conventional art in which a higher aliphatic tertiary amine or at least one selected from the group consisting of a chlorine agent, a bromine agent, and chlorine dioxide is used alone. Thus, the present invention was completed.

25 [0012]

The present invention relates to a method for preventing adhesion of marine organisms and slime to a seawater cooling water system, including adding a first chemical containing a higher aliphatic tertiary amine represented by the formula (I) and a second chemical containing at least one selected from the group consisting of a chlorine agent, a bromine agent, and chlorine dioxide to seawater of a seawater cooling water system,
[Chem. 1]



wherein substituents R¹, R² and R³ are the same as or different from one another and each are a C1 to C28 saturated or unsaturated aliphatic hydrocarbon group optionally replaced by one hydroxy or alkoxy group, with a total carbon number of R¹, R², and R³ being 10 to 37.

The method for preventing adhesion of marine organisms of the present invention preferably includes adding the first chemical to seawater of the seawater cooling water system for at least 12 hours a day such that the first chemical in the seawater has a concentration of 0.001 to 0.3 mg/L.

The method for preventing adhesion of marine organisms of the present invention preferably includes adding the second chemical to seawater of the seawater cooling water system for at least one hour a day such that the second chemical in the seawater has a concentration of 0.002 to 3.0 mg/L.

The chlorine agent or the bromine agent in the second chemical preferably includes (a) at least one substance that produces hypochlorous acid in water, selected from chlorine gas, calcium hypochlorite, sodium hypochlorite, chlorinated isocyanuric acid, sodium dichloroisocyanurate, potassium dichloroisocyanurate, sodium monochloroisocyanurate, potassium monochloroisocyanurate, sodium trichloroisocyanurate, and potassium trichloroisocyanurate, (b) at least one substance that produces hypobromous acid in water, selected from sodium hypobromite, a reaction product of sodium bromide and sodium hypochlorite, and bromine water, (c) a seawater electrolyte, or (d) at least one combined chlorine or

combined bromine, selected from monochloramine, dichloramine, trichloramine, monobromamine, dibromamine, tribromamine, N-chlorosulfamate, and N-bromosulfamate.
[0013]

5 The present invention also relates to an agent for preventing adhesion of marine organisms and slime for use in the method for preventing adhesion of marine organisms and slime, including, as active ingredients, at least one selected from the group consisting of chlorine agents,
10 bromine agents, and chlorine dioxide, and a higher aliphatic tertiary amine represented by the formula (I).
[0014]

 The present invention also relates to a kit for preventing adhesion of marine organisms and slime for use
15 in the method for preventing adhesion of marine organisms and slime, the kit including: a first chemical containing a higher aliphatic tertiary amine represented by the formula (I); and a second chemical containing at least one selected from the group consisting of chlorine agents, bromine
20 agents, and chlorine dioxide.

- Advantageous Effects of Invention
[0015]

 The method for preventing adhesion of marine
25 organisms and the like of the present invention, the agent and kit for preventing adhesion of marine organisms and the like for use in the method can prevent adhesion of a wide range of marine organism species (e.g., mussels such as blue mussels, barnacles, bryozoans, and other marine
30 organisms) and slime.

 Furthermore, according to the method for preventing adhesion of marine organisms and the like of the present invention, and the agent and kit for preventing adhesion of marine organisms and slime for use in the method, the
35 amount of the first chemical containing a higher aliphatic

tertiary amine represented by the formula (I) and the amount of the second chemical containing at least one selected from the group consisting of halogenated chemicals such as chlorine agents and bromine agents and chlorine dioxide can be reduced as compared with the case of using the first chemical or second chemical alone, while the effects of both the first chemical and the second chemical can be maintained for a long time.

In power plants, for example, chlorine agents or bromine agents are added to intake seawater to achieve the effect of preventing adhesion of marine organisms. However, due to regulations on the concentration of residual chlorine in wastewater, there may be a case where sufficient chlorine agents or bromine agents cannot be added, and the concentration of chlorine or bromine required in the heat exchanger (condenser) may not be kept, resulting in an insufficient effect of preventing adhesion of marine organisms. According to the present invention, addition of the first chemical containing a higher aliphatic tertiary amine to such a seawater system can provide a sufficient effect of preventing adhesion of marine organisms even within the regulations on the concentration of residual chlorine mentioned above.

According to the method for preventing adhesion of marine organisms and the like of the present invention, and the agent and kit for preventing adhesion of marine organisms and the like for use in the method, adhesion of a wide range of marine organism species (e.g., mussels such as blue mussels, barnacles, bryozoans, and other marine organisms) can be prevented in seawater cooling water systems that use large amounts of seawater, while the amounts of the first chemical and the second chemical used are reduced. Thus, excellent cost performance can be achieved with due considerations to the environment.

DESCRIPTION OF EMBODIMENTS

[0016]

(Method for preventing adhesion of marine organisms)

The method for preventing adhesion of marine
5 organisms and the like of the present invention includes
adding a first chemical containing a higher aliphatic
tertiary amine represented by the above formula (I) and a
second chemical containing at least one selected from the
group consisting of chlorine agents, bromine agents, and
10 chlorine dioxide to seawater in a seawater cooling water
system.

Preferably, the first chemical and the second
chemical are added to seawater of the seawater cooling
water system to concentrations that achieve both prevention
15 of adhesion of marine organisms and prevention of adhesion
of slime. The first chemical and the second chemical can
be added at the same or different times and in the same or
different locations.

[0017]

20 The "seawater cooling water system" as used herein
includes, in one or more embodiments, water intake
equipment and equipment to be cooled such as condensers and
heat exchangers, for example. The water intake equipment
includes water conduits, screens to remove foreign matter
25 from seawater, circulating water pumps (intake pumps), and
circulating water pipes (intake pipes).

The "seawater of the seawater cooling water system"
as used herein refers to seawater used as cooling water in
equipment to be cooled, such as condensers and heat
30 exchangers, for example.

The present invention can prevent adhesion of a wide
range of marine organism species (e.g., mussels such as
blue mussels, barnacles, bryozoans, and other marine
organisms) and slime to seawater cooling water systems,
35 while using smaller amounts of the first chemical and the

second chemical. Therefore, in seawater cooling water systems that use large amounts of seawater, the chemical concentration in the seawater that is constantly discharged can be kept to an extremely low level, while prevention of
5 adhesion of marine organism species and slime in the seawater cooling water systems is realized. Thus, excellent cost performance can be achieved with due considerations to the environment.

[0018]

10 The first chemical containing a higher aliphatic tertiary amine represented by the formula (I), which is added to seawater cooling water systems, shows an effect of preventing adhesion of large marine organisms such as mussels and barnacles to some degree, but an effect of
15 preventing adhesion is insufficient in some cases. The effect of preventing adhesion of stains by slime and the like is also sometimes insufficient. In contrast, the second chemical containing at least one selected from the group consisting of chlorine agents, bromine agents, and
20 chlorine dioxide shows an effect of preventing adhesion of stains by slime and the like but does not show or insufficiently shows an effect of preventing adhesion of large marine organisms such as mussels and barnacles.

 In the method for preventing adhesion of marine
25 organisms and the like of the present invention in which the first chemical and second chemical described above are used together, presumably, the first chemical and the second chemical can cover each other's shortcomings and maintain their effects for a long period of time,
30 preventing adhesion of a wide range of marine organism species and slime. In particular, when the concentrations of the first chemical and the second chemical in seawater are set within specific ranges, presumably, the effects of both chemicals can be maintained for a long period of time
35 without causing overuse of either one or both chemicals and

adhesion of a wide range of marine organism species and
slime can be prevented.

In other words, use of the first chemical and the
second chemical together is considered to have a
5 synergistic effect on prevention of adhesion of marine
organisms and adhesion of slime.
[0019]

In the technical field to which the present invention
belongs, the rule of thumb that combination of multiple
10 chemicals with different selectivity against attached
marine organisms and the like produces only superior
effects of the chemicals used is not clear, and it is not
known without actual confirmation. When chemicals with
selectivity against attached marine organisms are added to
15 seawater, attached marine organism species other than the
target organisms often increase and become dominant.
Therefore, in the technical field of the present invention,
it is not simply a matter of combining multiple chemicals
to obtain the combination of superior effects they have,
20 but rather, it is impossible to know what results will be
obtained without actually checking the outcome.
[0020]

In the present invention, the first chemical and the
second chemical should be added to locations where the
25 effects of preventing adhesion of marine organisms and
adhesion of slime can be obtained in the seawater cooling
water system.

The first chemical and the second chemical may be
added at the same or different locations in the seawater
30 cooling water system. In order to further improve the
effects of preventing adhesion of marine organisms and
slime, specific locations where the first chemical and the
second chemical are to be added are preferably the intake
and/or a vicinity of the intake of the intake pump, and the
35 inlet(s) of the heat exchanger and/or the condenser in the

seawater cooling water system. The same location in the seawater cooling water system means the same device, the same tank, and the same piping (piping between devices). The vicinity of the intake of the intake pump in the seawater cooling water system means the location where the chemical added can be taken into the intake.

[0021]

(First chemical)

[Higher aliphatic tertiary amine]

10 The higher aliphatic tertiary amine used in the method, agent, and kit for preventing adhesion of marine organisms and the like of the present invention is represented by the formula (I) in one or more embodiments.

[0022]

15 Specific examples of the higher aliphatic tertiary amine represented by the formula (I) used in the method, agent, and kit for preventing adhesion of marine organisms and the like of the present invention include octyldimethylamine, decyldimethylamine, dodecyldimethylamine tetradecyldimethylamine, 20 pentadecyldimethylamine, hexadecyldimethylamine, octadecyldimethylamine, icosyldimethylamine, docosyldimethylamine, coconut alkyldimethylamine, tallow alkyldimethylamine, hardened tallow alkyldimethylamine, didecylmethylamine, didodecylmethylamine, dioctadecylmethylamine, dioleoylmethylamine, di(tallow alkyl)methylamine, di(coconut alkyl)methylamine, dodecyl tetradecyl methylamine, dodecyl octadecyl methylamine, tetradecyl hexadecyl methylamine, dodecylmethylpropylamine, 25 tallow alkylethylpropylamine, tallow alkyldiethylamine, tallow alkyldipropylamine, tallow alkyldibutylamine, coconut-alkyldihexylamine, trioctylamine, tridecylamine, β -hydroxydodecyldimethylamine, β -hydroxyhexadecyldimethylamine, β -hydroxyoctadecyldimethylamine, di(β - 35

hydroxyhexadecyl)methylamine, di(β -
hydroxyoctadecyl)methylamine, tallow
alkyloxypropyldimethylamine, tallow
alkyloxypropyldiethylamine, 3-(2-
5 ethylhexyloxy)propyldimethylamine, 3-(2-
ethylhexyloxy)propyldiethylamine, 3-
dodecyloxyethyldimethylamine, 3-
dodecyloxyethyldiethylamine, 3-(coconut
alkyloxy)propyldimethylamine, and 3-(coconut
10 alkyloxy)propyldiethylamine.
[0023]

In the formula (I), the substituents R^1 and R^2 each
are more preferably a C1-C4 alkyl group, and the
substituent R^3 is more preferably a C8 to C22 saturated or
15 unsaturated linear aliphatic hydrocarbon group.
[0024]

Specific examples of the higher aliphatic tertiary
amine represented by the formula (I) that is more
preferably used include octyldimethylamine,
20 decyldimethylamine, dodecyldimethylamine,
tetradecyldimethylamine, pentadecyldimethylamine,
hexadecyldimethylamine, octadecyldimethylamine,
icosyldimethylamine, docosyldimethylamine,
dodecylmethylpropylamine, coconut alkyldimethylamine,
25 tallow alkyldimethylamine, hardened tallow
alkyldimethylamine, tallow alkyldiethylamine, tallow
alkyldipropylamine, tallow alkyldibutylamine, and tallow
alkylethylpropylamine.
[0025]

30 The "tallow alkyl group" and "hardened tallow alkyl
group" mainly refer to C16 to C18 saturated or unsaturated
linear aliphatic hydrocarbon groups. The "coconut alkyl
group" mainly refers to a C12 to C16 saturated or
unsaturated linear aliphatic hydrocarbon group. Compounds
35 containing the "tallow alkyl group," "hardened tallow alkyl

group," or "coconut alkyl group" are mixed aliphatic tertiary amines produced from tallow, hardened tallow, or coconut fat by known means.

[0026]

5 The higher aliphatic tertiary amine represented by the formula (I) may be used in the form of a salt of hydrochloric acid, hydrobromic acid, nitric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, oleic acid, naphthenic acid, adipic acid, lactic acid, citric
10 acid, saccharin, or the like.

 For example, in the case of an acetic acid salt, it can be obtained by reacting a higher aliphatic tertiary amine represented by the formula (I) with an equivalent molar amount of acetic acid.

15 When any of these compounds are added to the seawater cooling water system, it may be diluted or dissolved in seawater or freshwater as appropriate to a desired concentration.

[0027]

20 [Method of adding first chemical containing higher aliphatic tertiary amine represented by formula (I)]

 The first chemical containing a higher aliphatic tertiary amine represented by the formula (I) that can be used in the method, agent, and kit for preventing adhesion
25 of marine organisms and the like of the present invention is preferably used in the form of a water formulation prepared by dissolving the first chemical in water or in the form of an aqueous formulation prepared by dissolving the first chemical in a hydrophilic organic solvent such as
30 ethyl alcohol or isopropyl alcohol and water for ease of operation, transportation, handling, economy, and effectiveness.

[0028]

 The addition concentration of the first chemical
35 containing a higher aliphatic tertiary amine represented by

the formula (I) can be adjusted as appropriate with reference to the concentration of the first chemical in seawater of the seawater cooling water system in one or more embodiments. The concentration of the first chemical in the seawater is preferably 0.001 to 0.3 mg/L, more preferably 0.005 to 0.1 mg/L, still more preferably 0.01 to 0.03 mg/L in terms of the effect of preventing adhesion of marine organisms to the seawater cooling water system.

[0029]

The addition time for adding the first chemical tends to be inversely proportional to the addition concentration of the chemical. From the standpoint of preventing adhesion of marine organisms, the addition time is preferably at least 12 hours a day, more preferably at least 14 hours a day, still more preferably at least 16 hours a day within the above concentration range. The addition time may be at most 24 hours, at most 22 hours, or at most 20 hours a day (24 hours). Addition may be continuous or intermittent.

[0030]

The location where the first chemical is added is not limited, and may be, in one or more embodiments, any location before the intake seawater is pumped into the seawater cooling water system pipe by a pump or other means. From the standpoint of preventing troubles caused by adhesion of marine organisms, preferred is, for example, the vicinity of the intake of the intake pump, or the inlet of the heat exchanger or condenser.

[0031]

The concentration of the first chemical in seawater can be obtained, for example, by measuring the concentration in seawater at facilities to be cooled, such as condensers and heat exchangers, by a common measurement method.

[0032]

(Second chemical)

[Chlorine agent or bromine agent]

A chlorine or bromine agent that can be used in the method, agent, and kit for preventing adhesion of marine organisms of the present invention may be a known chlorine
5 or bromine agent. Examples thereof include:

(a) substances that produce hypochlorous acid in water such as chlorine gas, hypochlorite (e.g., calcium hypochlorite, sodium hypochlorite), chlorinated isocyanuric
10 acid, dichloroisocyanurate (e.g., sodium dichloroisocyanurate, potassium dichloroisocyanurate), monochloroisocyanurate (e.g., sodium monochloroisocyanurate, potassium monochloroisocyanurate), and trichloroisocyanurate (e.g., sodium
15 trichloroisocyanurate, potassium trichloroisocyanurate);

(b) substances that produce hypobromous acid in water, such as sodium hypobromite, a reaction product of sodium bromide and sodium hypochlorite, and bromine water;

(c) a seawater electrolyte (electrolyte containing hypochlorous acid obtained by electrolyzing seawater in an
20 electrolyzer); and

(d) combined chlorine (stabilized chlorine) and combined bromine (stabilized bromine) such as monochloramine, dichloramine, trichloramine, monobromamine, dibromamine, tribromamine, N-chlorosulfamate, and N-
25 bromosulfamate.

Among these, (a), (b) and (c) are preferred from practical viewpoints such as an effect of preventing adhesion of marine organisms, economic efficiency, and ease
30 of handling. From the viewpoint of industrial availability, particularly preferred are sodium hypochlorite and potassium hypochlorite. Preferred among (d) are monochloramine and monobromamine, followed by N-chlorosulfamate and N-bromosulfamate.

35 The term "chlorine agent" as used herein means any

known "chlorine agent" used in accordance with the common technical knowledge of the art in the technical field of the present invention, and does not include chlorine dioxide.

5 [0033]

N-Chlorosulfamate and N-bromosulfamate can be obtained by known methods, e.g., by using the methods disclosed in JP 2003-503323 T, JP 2006-022097 A, JP H11-506139 T, JP H11-506139 T, JP 2001-501869 T, JP 2003-507326
10 T, JP 2014-101251 A, JP 2017-159276 A, and other publications.

In the present invention, the reaction products of sulfamic acid with hypochlorous acid and/or hypobromous acid can be suitably used.

15 Combined chlorine, such as monochloramine, can be prepared by the methods disclosed in JP 4914146 B, JP 2017-119245 A, JP 2017-53054 A, and other publications.
[0034]

The chlorine agent and bromine agents may be diluted
20 or dissolved in seawater or freshwater to a desired concentration before use.

In the case where (a) a substance that produces hypochlorous acid in water or (c) a seawater electrolyte is added to seawater, hypochlorous acid reacts with bromide
25 ions present in the seawater, and chlorine and bromine are quickly replaced. For example, when sodium hypochlorite is added to seawater, it quickly becomes sodium hypobromite. Therefore, the effect of preventing adhesion of marine organisms is the same whichever of (a), (b), and (c) is
30 used.

[0035]

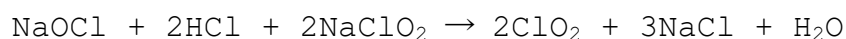
[Chlorine dioxide]

Chlorine dioxide, which can be used in the method, agent, and kit for preventing adhesion of marine organisms
35 and the like of the present invention, is an extremely

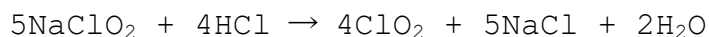
unstable chemical substance, making its storage and transportation very difficult. Therefore, it is preferable to produce (generate) chlorine dioxide on site by known methods and adjust it to the addition concentration before
 5 use.

For example, chlorine dioxide can be produced by the following reactions, and a commercial chlorine dioxide generator (device) can be used.

(1) Reaction of sodium hypochlorite with hydrochloric acid
 10 and sodium chlorite



(2) Reaction of sodium chlorite with hydrochloric acid



(3) Reaction of sodium chlorate, hydrogen peroxide, and
 15 sulfuric acid



[0036]

The second chemical that can be used in the method, agent, and kit for preventing adhesion of marine organisms
 20 and the like of the present invention should be set as appropriate in accordance with the condition of the seawater to which the second chemical is to be added, and at least one selected from the group consisting of chlorine agents, bromine agents, and chlorine dioxide is added
 25 preferably to a concentration of 0.002 to 3.0 mg/L in seawater of the seawater cooling water system.

The concentration of the second chemical in seawater means the "effective chlorine concentration" in the case where the second chemical includes a chlorine agent and/or
 30 a bromine agent.

When the concentration of the second chemical in seawater is lower than 0.002 mg/L, the effect of preventing adhesion of marine organisms and slime may be insufficient. When the concentration of the second chemical is higher
 35 than 3.0 mg/L, no further effect can be expected and is

undesirable from an economic standpoint.

The concentration of the second chemical is more preferably 0.01 to 1.0 mg/L, still more preferably 0.01 to 0.3 mg/L.

5 [0037]

The addition time of the second chemical may be set as appropriate in accordance with the addition concentration of the first chemical used in combination, the condition of the seawater to which the second chemical is to be added, and other factors, but is normally 1 to 24
10 hours a day.

When the addition time is shorter than one hour a day, the effect of preventing adhesion of marine organisms and slime owing to the combination with the first chemical
15 may possibly be insufficient.

The addition time of the second chemical is more preferably 1 to 22 hours a day.

When the addition concentration of the second chemical is 0.05 mg/L or higher, preferably 0.1 mg/L or
20 higher, more preferably 0.2 mg/L or higher, the addition time of the second chemical can be set to 1 to 5 hours, preferably 1 to 4 hours a day. With a relatively high addition concentration of the second chemical, the effect of the present invention can be achieved even when the
25 addition time is short. Moreover, a relatively high concentration and short addition time of the second chemical can provide an excellent effect of preventing adhesion of slime.

[0038]

30 The location where the second chemical is added is not limited, and in one or more embodiments, may be any location before the intake seawater is pumped into the seawater cooling water system piping by a pump or other means. From the standpoint of preventing troubles caused
35 by adhesion of marine organisms, preferred is, for example,

the vicinity of the intake of the intake pump, or the inlet of the heat exchanger or condenser.

[0039]

5 The concentration of the second chemical in seawater can be obtained, for example, by measuring the concentration in seawater at facilities to be cooled, such as condensers and heat exchangers, by a normal measurement method (e.g., DPD method).

[0040]

10 (Other additives)

In the method for preventing adhesion of marine organisms of the present invention, other additives known in the technical field may be used in combination, as long as they do not interfere with the effects of the invention.

15 Examples thereof include marine organism adhesion inhibitors such as dialkyl dithiocarbamate, ferrous metal corrosion inhibitors, and defoamers.

[0041]

(Addition method)

20 The chemicals may be added by methods using, for example, injection pumps, diffusion tubes, or sprayers. In the present invention, conventional physical means can be used to rapidly and substantially uniformly diffuse trace amounts of chemicals into the seawater cooling water
25 system. Specific examples thereof include installation of devices such as diffusers, agitators, and obstruction plates in the water system. Since these devices are included in the seawater cooling water system, they may be used as substitutes.

30

EXAMPLES

[0042]

The present invention is specifically described with reference to, but not limited to, the following test
35 examples.

[0043]

[Test Example 1]

The effect of preventing adhesion of marine organisms and the effect of preventing adhesion of slime were checked
5 in combination use of N,N-dimethyl tallow alkylamine (tallow alkyldimethylamine) as the first chemical, and one of a chlorine agent, a bromine agent, or chlorine dioxide as the second chemical.

A waterway test rig was set up at a certain location
10 on the coast of Wakayama Prefecture facing the Pacific Ocean, and the test was carried out.

Unfiltered seawater (pH 8) pumped by a submersible pump was divided into 19 channels (test sections) at a flow rate of 1 m³/h for 79 days in a transient manner, and the
15 chemicals prepared as mentioned below were added to the channels to the chemical concentrations shown in Table 1 over the daily addition time specified in Table 1.

The chemical concentration is the concentration set in an acrylic column for checking the effect of preventing
20 adhesion as described below, and the concentration of hypochlorite used as the chlorine agent is the effective chlorine concentration.

In addition, the amount of the chemical added was the same in test sections in which the chemical concentration
25 was the same. For example, the amount of chlorine dioxide added in Example 1 and Comparative Example 5 was the same, and the amount of hypochlorous acid added in Example 4 and Comparative Example 8 was the same.

[0044]

30 An acrylic column (inner diameter 64 mm x length 300 mm x thickness 2 mm, surface area 602.88 cm²) for checking the effect of preventing adhesion was placed in each channel, and a titanium tube (inner diameter 23.4 cm, length 1000 mm, wall thickness 10 mm) for checking the
35 effect of preventing adhesion of slime was inserted

immediately downstream of the acrylic column. The effects of the chemicals were evaluated by weighing the amount of organisms attached to the column and the wet volume of slime attached to the inner surface of the titanium tube
5 after completion of water flow.

The test was also conducted with no chemical added as a blank.

Table 1 shows the results obtained, along with the concentration of each chemical and the addition time
10 thereof.

[0045]

(Chemical added)

The higher aliphatic tertiary amine in the first chemical was N,N-dimethyl tallow alkylamine (C12 to C18),
15 the chlorine agent in the second chemical included sodium hypochlorite and monochloramine, the bromine agent in the second chemical was N-bromosulfamate, and chlorine dioxide in the second chemical was chlorine dioxide generated by mixing sodium chlorate and hydrochloric acid.

20 Specifically, N,N-dimethyl tallow alkylamine was adjusted to the chemical concentration for addition to seawater by diluting it with pure water as appropriate, and added using a metering pump from the front of the acrylic column for checking the effect of preventing adhesion.

25 Sodium hypochlorite was adjusted to the chemical concentration for addition to seawater by diluting a sodium hypochlorite solution having an effective chlorine concentration of 12% with pure water as appropriate, and was similarly added using a metering pump from the front of
30 the acrylic column for checking the effect of preventing adhesion.

Chlorine dioxide in the form of a chlorine dioxide solution was generated by mixing aqueous solutions of sodium chlorite and hydrochloric acid, each diluted with
35 pure water as appropriate, in the tube before the chemical

addition point such that the chlorine dioxide concentration shown in Table 1 was achieved and allowing a residence time of one hour. The aqueous solution was added from the front of the acrylic column for checking the effect of preventing
5 adhesion. Preliminary tests had confirmed the generation of chlorine dioxide and also confirmed that sodium chlorite did not remain at a concentration that would affect its effectiveness.

Monochloramine and N-bromosulfamate were each
10 generated by known methods (e.g., methods disclosed in JP 2017-53054 A and JP 2017-159276 A), adjusted to the chemical concentration for addition to seawater by diluting with pure water as appropriate, and added using a metering pump from the front of the acrylic column for checking the
15 effect of preventing adhesion.

[0046]

(Checking of effect for preventing adhesion of marine organisms)

After the test, the mass W1 (g) of the column removed
20 from the channel was measured. The amount of attached organisms (g) was calculated by the following equation using the mass W0 of the column when dry measured before the test.

Amount of attached organisms (g) = W1 - W0

25 The attached organisms in the blank were mainly derived from marine organisms including mussels such as blue mussels, barnacles, and bryozoans. Also attached were excrement and carcasses of attached organisms and slime, organic-rich detritus-like materials such as extracellular
30 secretions, and viscous particles and suspended solids contained in seawater, which were also included in the amount of attached organisms.

Based on the adhesion of marine organisms in the blank, the effect of preventing adhesion of marine
35 organisms is considered sufficient when the amount of

attached organisms is 15 g or less in the present test example.

(Checking of effect of preventing adhesion of slime)

After the test, the slime adhering to the inner
5 surface of the titanium tube removed from the channel was
scraped off, collected in a 100-mL colorimetric tube, and
left to stand for four hours. The effect of preventing
adhesion was evaluated by weighing the wet volume after the
standing.

10 The slime scraped in the blank was mainly derived
from microorganisms attached to the titanium tube. Similar
to the checking of the effect of preventing adhesion in the
column, the slime attached to the inner surface of the
titanium tube also contained detritus-like substances.
15 However, since the diameter of the titanium tube was
approximately 1/3 of the column diameter and the velocity
of the seawater cooling water in the titanium tube was
faster, it was confirmed that there was no adhesion of
mussels such as the blue mussels, barnacles, bryozoans, or
20 other attached marine organisms.

Based on the slime adhesion situation in the blank,
the effect of preventing adhesion of slime is considered
sufficient when the slime volume is 10 mL or less in the
present test example.

25 [0047]

[Table 1]

	First chemical			Second chemical			Prevention of adhesion of marine organisms	Prevention of adhesion of slime
	Higher aliphatic tertiary amine			Chlorine agent, bromine agent, or chlorine dioxide				
	Chemical	addition time /day	Concentration	Chemical	addition time /day	Concentration		
Example 1	N,N-Dimethyl tallow alkylamine	16 h	0.01	Chlorine dioxide	16 h	0.015	8.5	3.8
Example 2	N,N-Dimethyl tallow alkylamine	20 h	0.01	Chlorine dioxide	22 h	0.01	7.7	8.5
Example 3	N,N-Dimethyl tallow alkylamine	20 h	0.02	Chlorine dioxide	1 h	0.3	4.9	2.2
Example 4	N,N-Dimethyl tallow alkylamine	18 h	0.01	Hypochlorous acid	20 h	Residual salt 0.01	4.3	7.3
Example 5	N,N-Dimethyl tallow alkylamine	18 h	0.02	Hypochlorous acid	2 h	Residual salt 0.3	8.7	2.1
Example 6	N,N-Dimethyl tallow alkylamine	18 h	0.02	Monochloramine	2 h	Residual salt 0.3	9.3	1.8
Example 7	N,N-Dimethyl tallow alkylamine	16 h	0.03	N-Bromosulfamate	4 h	Residual salt 0.2	8.7	2.6
Comparative Example 1	N,N-Dimethyl tallow alkylamine	20 h	0.025		-		16.1	13.8
Comparative Example 2	N,N-Dimethyl tallow alkylamine	20 h	0.02		-		43.0	16.0
Comparative Example 3	N,N-Dimethyl tallow alkylamine	20 h	0.01		-		93.1	19.2
Comparative Example 4	N,N-Dimethyl tallow alkylamine	16 h	0.03		-		38.6	15.6
Comparative Example 5	-			Chlorine dioxide	16 h	0.015	21.0	5.6
Comparative Example 6	-			Chlorine dioxide	22 h	0.01	35.1	12.8
Comparative Example 7	-			Chlorine dioxide	1 h	0.3	32.6	3.9
Comparative Example 8	-			Hypochlorous acid	20 h	Residual salt 0.01	29.8	10.6
Comparative Example 9	-			Hypochlorous acid	2 h	Residual salt 0.3	36.9	1.8
Comparative Example 10	-			Monochloramine	2 h	Residual salt 0.3	40.1	2.5
Comparative Example 11	-			N-Bromosulfamate	4 h	Residual salt 0.2	44.8	4.0
Reference example (blank)					-		146.7	21.9

[0048]

The results in Table 1 above confirm the following.

(1) Comparative examples 1, 2, 3, and 4, in which N,N-dimethyl tallow alkylamine was used alone as the first chemical, compared to the blank (reference example) to which no chemical was added, showed the effect of preventing adhesion of marine organisms to some degree, but the effect was insufficient. The effect of preventing adhesion of slime was also insufficient.

(2) In contrast, in Example 3 in which N,N-dimethyl tallow alkylamine was added in an amount of 0.02 mg/L (20 h) as in Comparative Example 2, Example 2 in which N,N-dimethyl tallow alkylamine was added in an amount of 0.01 mg/L (20 h) as in Comparative Example 3, and Example 7 in which N,N-dimethyl tallow alkylamine was added in an amount of 0.03 mg/L (16 h) as in Comparative Example 4, a sufficient effect of preventing adhesion of marine organisms and a sufficient effect of preventing adhesion of slime were confirmed as the second chemical was used in combination in these examples.

(3) In Comparative Examples 5, 7, and 9 to 11, in which the second chemical was used alone, a sufficient effect of preventing adhesion of slime was confirmed but the effect of preventing adhesion of marine organisms was insufficient. In Comparative Examples 6 and 8, both the effect of preventing adhesion of slime and the effect of preventing adhesion of marine organisms were insufficient. The results of Comparison Examples 6 and 7, and Comparative Examples 8 and 9 also show that addition of the second chemical at a somewhat higher concentration for a shorter time exhibits a higher effect of preventing adhesion of slime compared to addition of the second chemical at a lower concentration for a longer time.

(4) The results of Examples 1 to 7 confirmed that, when the first chemical and the second chemical are used in combination, addition of the first chemical at an addition

concentration of 0.01 to 0.03 mg/L for 16 to 20 hours a day
and addition of the second chemical at an addition
concentration of 0.01 to 0.3 mg/L for 1 to 22 hours a day
give a sufficient effect of preventing adhesion of marine
5 organisms and a sufficient effect of preventing adhesion of
slime.

(5) The results in Table 1 show that combination use
of, as the first chemical, N,N-dimethyl tallow alkylamine
and, as the second chemical, a chlorine agent such as
10 chlorine dioxide, sodium hypochlorite, or monochloramine
and a bromine agent such as N-bromosulfamate can prevent
adhesion of a wider range of marine organisms (e.g.,
mussels such as blue mussels and green-lipped mussels,
barnacles, bryozoans, and other marine organisms) as well
15 as slime, compared to the use of either the first chemical
or the second chemical alone.

It was also confirmed that combination use of the
first chemical and the second chemical gives sufficient and
sustained effect of preventing adhesion of marine organism
20 and slime for 79 days without increasing the amount of both
chemicals used.

[0049]

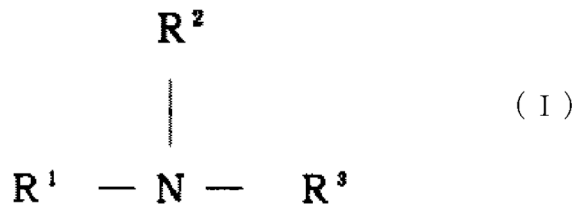
Based on the above results, it was confirmed that the
method, agent, and kit for preventing adhesion of marine
25 organisms and the like of the present invention can prevent
adhesion of a wide range of marine organism species (e.g.,
mussels such as blue mussels, barnacles, bryozoans, and
other marine organisms) and slime for a long period of time
while using smaller amounts of the first chemical and the
30 second chemical added to the seawater cooling water system.

CLAIMS

Claim 1. A method for preventing adhesion of marine organisms and slime to a seawater cooling water system,
 5 comprising

adding a first chemical containing a higher aliphatic tertiary amine represented by the formula (I) and a second chemical containing at least one selected from the group consisting of a chlorine agent, a bromine agent, and
 10 chlorine dioxide to seawater of a seawater cooling water system:

[Chem. 1]



wherein substituents R^1 , R^2 and R^3 are the same as or
 15 different from one another and each are a C1 to C28 saturated or unsaturated aliphatic hydrocarbon group optionally replaced by one hydroxy or alkoxy group, with a total carbon number of R^1 , R^2 , and R^3 being 10 to 37.

20 Claim 2. The method for preventing adhesion of marine organisms and slime according to claim 1, comprising

adding the first chemical to seawater of the seawater cooling water system for at least 12 hours a day such that the first chemical in the seawater has a concentration of
 25 0.001 to 0.3 mg/L.

Claim 3. The method for preventing adhesion of marine organisms and slime according to claim 1 or 2, comprising

adding the second chemical to seawater of the seawater cooling water system for at least one hour a day
 30 such that the second chemical in the seawater has a

concentration of 0.002 to 3.0 mg/L.

Claim 4. The method for preventing adhesion of marine organisms and slime according to claim 1, 2, or 3,

5 wherein the chlorine agent or the bromine agent in the second chemical includes

 (a) at least one substance that produces hypochlorous acid in water, selected from chlorine gas, calcium hypochlorite, sodium hypochlorite, chlorinated isocyanuric acid, sodium dichloroisocyanurate, potassium
10 dichloroisocyanurate, sodium monochloroisocyanurate, potassium monochloroisocyanurate, sodium trichloroisocyanurate, and potassium trichloroisocyanurate,

 (b) at least one substance that produces hypobromous acid in water, selected from sodium hypobromite, a reaction product of sodium bromide and sodium hypochlorite, and
15 bromine water,

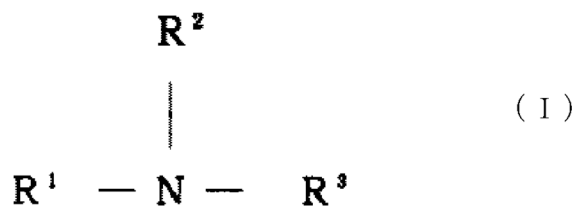
 (c) a seawater electrolyte, or

 (d) at least one combined chlorine or combined
20 bromine, selected from monochloramine, dichloramine, trichloramine, monobromamine, dibromamine, tribromamine, N-chlorosulfamate, and N-bromosulfamate.

Claim 5. An agent for preventing adhesion of marine organisms and slime for use in the method for preventing
25 adhesion of marine organisms and slime according to claim 1, 2, 3, or 4, the agent comprising, as active ingredients,

 at least one selected from the group consisting of chlorine agents, bromine agents, and chlorine dioxide, and
30 a higher aliphatic tertiary amine represented by the formula (I):

[Chem. 2]



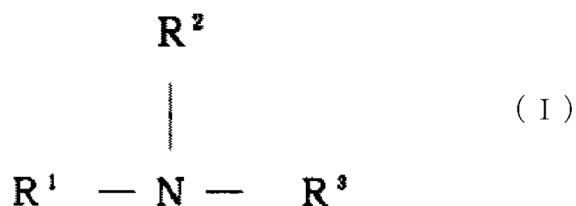
wherein substituents $\mathbf{R}^1$, $\mathbf{R}^2$, and $\mathbf{R}^3$ are the same as or different from one another, and each are a C1-C28 saturated or unsaturated aliphatic hydrocarbon group optionally
 5 replaced by one hydroxy or alkoxy group, with a total carbon number of $\mathbf{R}^1$, $\mathbf{R}^2$, and $\mathbf{R}^3$ being 10 to 37.

Claim 6. A kit for preventing adhesion of marine organisms and slime for use in the method for preventing
 10 adhesion of marine organisms and slime according to claim 1, 2, 3, or 4, the kit comprising:

a first chemical containing a higher aliphatic tertiary amine represented by the formula (I); and

a second chemical containing at least one selected
 15 from the group consisting of chlorine agents, bromine agents, and chlorine dioxide:

[Chem. 3]



wherein substituents $\mathbf{R}^1$, $\mathbf{R}^2$ and $\mathbf{R}^3$ are the same as or
 20 different from one another, and each are a C1-C28 saturated or unsaturated aliphatic hydrocarbon group optionally replaced by one hydroxy or alkoxy group, with a total carbon number of $\mathbf{R}^1$, $\mathbf{R}^2$, and $\mathbf{R}^3$ being 10 to 37.