

## DESCRIPTION

### METHOD OF INHIBITING FOAMING IN SEAWATER COOLING WATER SYSTEM

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#### TECHNICAL FIELD

The present invention relates to a method of inhibiting foaming in a seawater cooling water system. The present invention enables to efficiently inhibit the foaming in the seawater cooling water system that prevents deposition of marine organisms by the addition of a chlorine-generating agent.

#### BACKGROUND ART

In thermal power plants, steel plants, petroleum refining plants, petrochemical plants, other chemical plants and the like where seawater is used as cooling water, problems arise such as a reduction in cooling function caused by deposition of marine organisms in a cooling water system, and corrosion of a metallic material of a structure of the cooling water system such as a conducting tube and the like. In general, these problems have been dealt with by the addition of a marine organism anti-deposition agent and an anticorrosion agent to the cooling water system.

Examples of the marine organism anti-deposition agent that has widely been used include a chlorine-generating agent such as sodium hypochlorite, chlorine dioxide, chlorine gas and the like. However, in the case where such chlorine-generating agent was added to the above-described cooling water system, problems have sometimes arisen such as corrosion of a structure of the cooling water system, and

bubbling (foaming) due to a reaction with microorganisms and organic substances in seawater. More specifically, the foaming causes an adverse effect on operation of the cooling water system and also becomes a cause of a quality deterioration of products.

5           In a water system that is troubled with foaming, a silicon-based antifoam agent is generally used.

          Also, it has been known to use the silicon-based antifoam agent in combination with a higher aliphatic amine for the purpose of inhibiting foaming of a quaternary ammonium compound known as an agricultural  
10   chemical and an industrial disinfectant (see Japanese Examined Patent Publication No. 2713509 (Patent Document 1)).

          Also, Japanese Unexamined Patent Publication No. HEI 10(1998)-120508 (Patent Document 2) discloses a method wherein when disorders caused by marine organisms are prevented by the addition of a  
15   higher aliphatic tertiary amine or a salt thereof to a seawater cooling water system, transparency of seawater is measured and the addition of the amine is controlled based on changes of the transparency, and discloses that the higher aliphatic tertiary amine has difficulty in foaming in the seawater as compared to other amines.

20           However, the above-mentioned documents do not disclose that a higher aliphatic tertiary amine is effective at preventing foaming caused by a reaction with microorganisms and organic substances in seawater, and this effect has not been known.

          Patent Document 1: Japanese Examined Patent Publication No.  
25   2713509

          Patent Document 2: Japanese Unexamined Patent Publication No. HEI 10(1998)-120508

## DISCLOSURE OF THE INVENTION

### Problems that the Invention is to Solve

The present invention has an object of providing a method of inhibiting foaming in a seawater cooling water system which is capable of efficiently inhibiting the foaming generated in the seawater cooling water system in which deposition of marine organisms is prevented by the addition of a chlorine-generating agent.

### Means for Solving the Problems

As a result of studying diligently so as to solve the above-mentioned problems, the inventors of the present invention have found that it is possible to efficiently inhibit the foaming by adding a specific higher aliphatic tertiary amine to the seawater cooling water system in which the foaming is generated after the chlorine-generating agent is added, and have come to achieve the present invention.

Thus, the present invention provides the method of inhibiting the foaming in the seawater cooling water system, characterized in that the higher aliphatic tertiary amine is added to the seawater cooling water system to which the chlorine-generating agent is added, so that the foaming is inhibited in the seawater cooling water system.

### Effects of the Invention

According to the present invention, it is possible to provide the method of inhibiting the foaming in the seawater cooling water system which is capable of efficiently inhibiting the foaming generated in the seawater cooling water system in which the deposition of the marine organisms is prevented by the addition of the chlorine-generating agent.

The present invention is applicable to foaming generated in

seawater cooling water systems in thermal power plants, steel plants, petroleum refining plants, petrochemical plants, other chemical plants and the like, and is considerably useful industrially.

## 5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing a circulation device for antifoam test, used in Test Example 1.

Fig. 2 is a diagram showing changes of heights of foaming with time in Test Example 1.

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### Explanation of Reference Numerals

- |    |   |                                      |
|----|---|--------------------------------------|
|    | 1 | circulation device for antifoam test |
|    | 2 | container                            |
|    | 3 | pipe heater                          |
| 15 | 4 | tripod drain board                   |
|    | 5 | test seawater                        |
|    | 6 | pump (P)                             |
|    | 7 | pipe                                 |
|    | 8 | pipe outlet                          |

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## BEST MODE FOR CARRYING OUT THE INVENTION

The method of inhibiting the foaming in the seawater cooling water system of the present invention is characterized in that the higher aliphatic tertiary amine is added to the seawater cooling water system to which the chlorine-generating agent is added, so that the foaming is inhibited in the seawater cooling water system.

In the present invention, "a seawater cooling water system to which a chlorine-generating agent is added" means, for example, a

seawater cooling water system to which a chlorine-generating agent has been added for the purpose of preventing deposition of marine organisms.

Therefore, the present invention is suitably used for the seawater cooling water systems in the thermal power plants, the steel plants, the petroleum refining plants, the petrochemical plants, the other chemical plants and the like where seawater is used as cooling water and a chlorine-generating agent is added for the purpose of preventing deposition of marine organisms.

In the present invention, examples of the higher aliphatic tertiary amine to be added to the seawater cooling water system include known amines having 12 to 24 carbon atoms. Specific examples thereof include N,N-dimethyldodecylamine (= N,N-dimethylaurylamine), N,N-dimethyltetradecylamine, N,N-dimethylpentadecylamine, N,N-dimethylhexadecylamine, N,N-dimethylpentadecylamine, N,N-dimethyloctadecylamine, N,N-dimethyldocosylamine (= N,N-dimethylbehenylamine), N,N-dimethylpalmalkylamine and the like. These may be used alone or as a mixture (mixed alkylamine) of two or more kinds.

Examples of the mixed alkylamine include N,N-dimethyltallowalkylamine and N,N-dimethyl hardened tallowalkylamine and the like. These amines mean a mixture of amines, each of which is made from beef fat by known means and contains as a main component a saturated or unsaturated straight chain aliphatic hydrocarbon group having 12 to 18 carbon atoms.

In the method of the present invention, N,N-dimethylaurylamine, N,N-dimethylbehenylamine and N,N-dimethyltallowalkylamine are particularly preferred among the above-mentioned amines, from the viewpoint of a foaming inhibition effect.

The higher aliphatic tertiary amine 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 acid, saccharine and the like.

5           For example, it is possible to obtain an acetate by a reaction of the higher aliphatic tertiary amine with acetic acid in an equimolar amount.

When these are added to the seawater cooling water system, the compounds may appropriately be diluted with or dissolved in seawater or fresh water so that desired concentrations will be obtained.

10           In the present invention, a concentration of the higher aliphatic tertiary amine to be added to the seawater cooling water system may preferably be 0.005 to 5 mg/L, particularly preferably 0.01 to 1 mg/L, from the viewpoint of the foaming inhibition effect, though it depends on a water temperature and an effective chlorine concentration of the  
15 chlorine-generating agent present in the seawater cooling water system.

The chlorine-generating agent in the seawater cooling water system of the present invention to which the chlorine-generating agent has been added includes known chlorine-generating agents used for the purpose of preventing the deposition of the marine organisms, such as a  
20 hypochlorous acid and its salt, dichloroisocyanuric acid and its salt, a bleaching liquid  $[(\text{CaClO})_2]$ , chlorine dioxide, a chlorine gas obtainable by electrolysis of seawater and the like.

The method of inhibiting the foaming in the seawater cooling water system of the present invention efficiently inhibits the foaming  
25 when an effective concentration of the chlorine-generating agent present in the seawater cooling water system is 0.01 to 10 mg/L, preferably 0.05 to 50 mg/L in an effective chlorine concentration equivalent.

The method of inhibiting the foaming in the seawater cooling

water system of the present invention enables to prevent corrosion of a metallic material of a structure such as a conducting tube of the seawater cooling water system by way of addition of a compound which generates iron ions in water to the seawater cooling water system together with the  
5 higher aliphatic tertiary amine.

Examples of the compound which generates the iron ions in water include a compound that is soluble in water and capable of forming iron ions in water, such as ferrous sulfate, ferrous chloride, ammonium ferrous sulfate and the like. It may also include iron ions disclosed in  
10 Japanese Examined Patent Publication No. SHO 54(1979)-40472, generated by an iron ion generating device.

When these are added to the seawater cooling water system, the compounds may appropriately be diluted with or dissolved in seawater or fresh water so that desired concentrations will be obtained.

15 A concentration of the iron ions may preferably be 0.01 to 3 mg/L, particularly preferably 0.03 to 1 mg/L, from the viewpoint of an anticorrosion effect on metallic material.

The method of inhibiting the foaming in the seawater cooling water system of the present invention includes, as an example, a method  
20 of repeating intermittent addition of the chlorine-generating agent, addition of the higher aliphatic tertiary amine within 1 to 2 hours after the addition of the chlorine-generating agent, and addition of the chlorine-generating agent within 10 to 180 minutes after the addition of the higher aliphatic tertiary amine. This method is preferred since the  
25 method enables to achieve the efficient foaming inhibition effect, and corrosion of piping in the seawater cooling water system is difficult to occur. Since a similar effect is expected from a method of simultaneously adding a chlorine-generating agent and a higher aliphatic

tertiary amine to a seawater cooling water system in which a residual chlorine concentration at the time of discharging is controlled so that the concentration is maintained below a detection limit, such a method is also preferred.

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#### Examples

The present invention will be hereinafter described in detail with reference to preparation examples and test examples, but is not limited to these preparation and test examples.

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#### Preparation Example 1 (Preparation of Sodium Hypochlorite Aqueous Solution)

A 12% sodium hypochlorite aqueous solution was diluted with pure water, and a sodium hypochlorite aqueous solution having an effective chlorine concentration of 2000 mg/L was prepared.

#### Preparation Examples 2 to 7

Each of various amines listed below was reacted with acetic acid in an equimolar amount, and an acetate aqueous solution of each amine having a concentration of 2000 mg/L was prepared.

(Preparation Example 2) N,N-dimethyltallowalkylamine (C = 12 to 18)  
[dimethylalkyl tertiary amine]

manufactured by Lion Akzo Co., Ltd.; product name: Armeen  
DMTD

25 (Preparation Example 3) N,N-dimethylaurylamine (C = 12)

[dimethylalkyl tertiary amine]

manufactured by Lion Akzo Co., Ltd.; product name: Armeen  
DM12D

(Preparation Example 4) N,N-dimethylbenzylamine (C = 22)

[dimethylalkyl tertiary amine]

manufactured by Lion Akzo Co., Ltd.; product name: Armeen  
DM22D

5 (Preparation Example 5) dimethyloctylamine (C = 8)

[dimethylalkyl tertiary amine]

manufactured by Kao Corporation; product name: Farmin  
DM0898

(Preparation Example 6) di-hardened tallowalkylamine (C = 14 to 18)

10 [dialkyl secondary amine]

manufactured by Lion Akzo Co., Ltd.; product name: Armeen 2HT

(Preparation Example 7) octadecylamine (C = 18)

[alkyl primary amine]

manufactured by Wako Pure Chemical Industries, Ltd.; reagent

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#### Test Example 1 (Test to Check Foaming Heights)

By use of a circulation device 1 for an antifoam test shown in Fig.  
1, a test to check foaming heights was conducted according to the  
method of inhibiting the foaming in the seawater cooling water system of  
20 the present invention.

The sodium hypochlorite aqueous solution of Preparation  
Example 1 was added to seawater so as to obtain sodium hypochlorite  
having an effective chlorine concentration of 1.0 mg/L, thereby obtaining  
2 L of test seawater (pH 8.5).

25 Subsequently, the test seawater 5 was poured into a cylindrical  
container 2 which is made from vinyl chloride and provided with a pipe  
heater 3 (manufactured by Hakko Electric Machine Co., Ltd.; voltage: 100  
V; power consumption: 500 W) and a tripod drain board 4 (outer

diameter: 12 cm; height: 7 cm), and then the pipe heater 3 was heated so that a water temperature of the test seawater 5 increases to 40°C. Subsequently, the acetate aqueous solution of the amine of Preparation Example 2 was added to the test seawater by use of a micro-pipette so as to obtain an amine concentration of 0.1 mg/L, and then the solution was gently stirred.

After that, a pump 6 (magnet pump manufactured by Iwaki Co., Ltd.; type: MD-30R-N) in which a circulation flow rate had previously been adjusted to be 24 L/min was operated so as to suck the test seawater 5 from the bottom of the container 2, the test seawater 5 was dropped through a pipe 7 (inner diameter: 13 mm, path length: about 70 cm; height between a highest part of the pipe to a reference liquid surface: 20 cm) from a position (pipe outlet 8) where is 8.5 cm above the reference liquid surface, and the test seawater 5 was circulated for 300 seconds (see the arrows in Fig. 1). The foaming heights (each of which is a height from the reference liquid surface to an upper edge of the foaming) were measured at a time of 10 seconds, 30 seconds, 60 seconds, 90 seconds, 120 seconds, 180 seconds, 240 seconds and 300 seconds each after the circulation started.

Tests to check foaming heights were conducted in the same manner as described above, except for the use of the acetate aqueous solutions of the amines of Preparation Examples 3 to 7 respectively in place of the acetate aqueous solution of the amine of Preparation Example 2.

Also, a test to check a foaming height was conducted in the same manner as describe above, except an acetate solution of amine was not used, as a blank test.

Obtained results are shown in Fig. 2. In this figure, upper ● and

lower ● between 0 and 300 seconds indicate Preparation Example 3 and Preparation Example 2 respectively, and upper ● and lower ● between 300 and 600 seconds indicate Preparation Example 2 and Preparation Example 3 respectively.

5           From the results shown in Fig. 1, it is found that Preparation Examples 2 to 4 exhibit a most excellent foaming inhibition effect before and after termination of the circulation. Also, it is found that a foaming amount of Preparation Examples 5 and 6 each during the circulation is higher than that of the blank test, and the foaming amount of  
10 Preparation Examples 5 and 6 each before and after the termination of the circulation is much more than that of the blank test. Preparation Example 7 generated foaming with relatively high viscosity, and the foaming also adhered to a wall surface of a container.

#### 15 Test Example 2 (Test to Check an Antifoam Effect in Oil Factory)

          The test was conducted by use of a seawater cooling water system (water amount: 5000 tons/hour) in a certain oil factory where a chlorine treatment is performed, in which sodium hypochlorite is added to seawater near a water intake opening so as to obtain an effective chlorine  
20 concentration of 0.1 mg/L which prevents deposition of marine organisms in the water system. Before the test, foaming was observed at a water discharge opening.

          More specifically, the drug of Preparation Example 2 was added to the seawater near the water discharge opening of the seawater cooling  
25 water system so as to obtain a higher aliphatic tertiary amine having a concentration of 0.1 mg/L, and foaming at the water discharge opening was observed in 1 hour.

          Seawater collected before the test contained abundant diatoms

(Eucampia. sp), and water quality thereof was as follows.

[Quality of Seawater]

Suspended substance (ss): 30 mg/L

5 COD: 4.5 mg/L

pH: 8.1

The foaming that had been generated was inhibited by the addition of the drug of Preparation Example 2.

Also, since a large amount of foaming was observed when the  
10 diatoms were abundant, it is considered that a viscous substance secreted from the diatoms that were damaged by the chlorine treatment is deeply involved in the generation of the foaming.

## CLAIMS

1. A method of inhibiting foaming in a seawater cooling water system, characterized in that a higher aliphatic tertiary amine is added to the seawater cooling water system to which a chlorine-generating agent is added, so that the foaming is inhibited in the seawater cooling water system,

wherein, the higher aliphatic tertiary amine is N,N-dimethylaurylamine, N,N-dimethylbehenylamine, or N,N-dimethyltallowalkylamine.

2. The method of inhibiting the foaming in the seawater cooling water system according to claim 1, wherein a concentration of the higher aliphatic tertiary amine is 0.005 to 5 mg/L.

3. The method of inhibiting the foaming in the seawater cooling water system according to any one of claims 1 to 2, wherein an effective concentration of the chlorine-generating agent is 0.01 to 10 mg/L in an effective chlorine concentration equivalent.