METHOD OF PREVENTING METAL CORROSION IN COOLING WATER SYSTEM

Field of Invention

[0001]

The present invention relates to a method of preventing corrosion of a metal member in a cooling water system in which phosphorus cannot be used because of environmental regulations or the like and zinc is used as a corrosion-preventing component in the case where water treatment is performed in the cooling water system.

Background of Invention

[0002]

Metal corrosion in cooling water systems can cause serious economic problems, such as a decrease in production efficiency and emergency shutdown of plants. Accordingly, various methods have been proposed to prevent corrosion of metals in cooling water systems. As a method of preventing metal corrosion, high-concentration addition of phosphorus and zinc is generally performed.

However, with the recent tightening of environmental regulations, there has been an increase in the number of cases where phosphorus cannot be used in cooling water systems. As countermeasures against this, various non-phosphorus, non-zinc treatments and non-phosphorus, zinc treatments have been performed. However, the corrosion-

preventing effects of these treatments are insufficient compared with phosphorus and zinc treatments in many cases.

[0003]

Regarding the copolymers used in the present invention, the following reports have been made available. However, none of them is related to the use of copolymers in cooling water systems in which a non-phosphorus, zinc treatment is performed.

[0004]

Patent Literature 1 describes a method of preventing metal corrosion using a copolymer of a carboxyl group-containing monomer and a sulfone group-containing monomer, a copolymer of maleic acid and an alkene, and an azole compound in combination in a cooling water system in which a non-phosphorus, non-zinc treatment is performed. However, Patent Literature 1 does not specifically describe the case where a zinc compound is used together with copolymers.

[0005]

Patent Literatures 2 and 3 describe the corrosion-preventing effects of a copolymer, such as a terpolymer of acrylic acid/acrylamide methylpropanesulfonic acid/isobutylene, or silica scale-inhibiting effects in a cooling water system in which a non-phosphorus, non-zinc treatment is performed. However, Patent Literatures 2 and 3 do not relate to a combination of polymers and a zinc

compound being used together.

[Patent Literature]

[Patent Literature 1] WO2005/123981

[Patent Literature 2] Japanese Patent Publication 7-268666 A

[Patent Literature 3] Japanese Patent 3055815

Object and Summary of Invention

[0006]

It is an object of the present invention to provide a method of preventing metal corrosion in a cooling water system, which is a method of effectively inhibiting corrosion of a metal member in a cooling water system in which a non-phosphorus, zinc treatment is performed.

[0007]

The present inventors have performed thorough studies in order to solve the problem described above, and have found that, by using two types of copolymers having a specific functional group exhibiting a metal corrosion-preventing effect and a zinc compound in combination, the corrosion-preventing effect is markedly improved compared with the case where a treatment is performed using any one of the components alone.

[0008]

The present invention has been achieved on the basis of the finding described above. A method of preventing metal

corrosion in a cooling water system according to the present invention (claim 1), which is a method of preventing corrosion of a metal member in a cooling water system in which a non-phosphorus, zinc treatment is performed, includes causing the following components (A), (B), and (C) to be present in the water system:

(A) a copolymer of acrylic acid and a sulfone group-containing monomer (hereinafter described as the "copolymer (A)"),

(B) a copolymer of maleic acid and isobutylene (hereinafter described as the "copolymer (B)"), and

(C) a zinc compound.

[0009]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to Claim 1, the sulfone group-containing monomer of the copolymer (A) may be 2-acrylamide-2-methylpropanesulfonic acid and/or 3-allyloxy-2-hydroxypropanesulfonic acid.

[0010]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to Claim 1 or 2, the molecular weight of the copolymer (A) may be 500 to 50,000, and the molar ratio of acrylic acid to the sulfone group-containing monomer may be 7:3 to 9:1.

[0011]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to any one of Claims 1 to 3, the molecular weight of the copolymer (B) may be 10,000 to 50,000, and the molar ratio of maleic acid to isobutylene may be 5:5 to 8:2.

[0012]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to any one of Claims 1 to 4, the zinc compound may be zinc chloride and/or zinc sulfate.

[0013]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to any one of Claims 1 to 5, the copolymer (A) and the copolymer (B) may be added in the amount of 5 to 50 mg-solid content/L in total relative to the blow water amount of the water system.

[0014]

In the method of preventing metal corrosion in a cooling water system of the present invention, according to any one of Claims 1 to 6, the zinc compound may be added in the amount of 0.5 mg/L or more relative to the blow water amount of the water system.

[0015]

In the method of preventing metal corrosion in a

cooling water system of the present invention, according to any one of Claims 1 to 7, the calcium hardness of the water system may be 100 to 1,000 mg-$CaCO_3$/L, and the concentration of corrosive ions (total of the concentration of chloride ions and the concentration of sulfate ions) may be 2,000 mg/L or less.

Advantageous Effects of Invention

[0016]

According to the present invention, by using the copolymer (A), the copolymer (B), and the zinc compound in combination, corrosion of a metal member in a cooling water system in which a non-phosphorus, zinc treatment is performed can be effectively inhibited. That is, according to the present invention, while the anode reaction of a corroding portion is inhibited by carboxyl groups contained in the copolymer (A) and the copolymer (B), the cathode reaction is inhibited by the zinc compound, and furthermore, the zinc compound can be maintained in water by the action of sulfone groups of the copolymer (B), thus providing a very good effect of synergizing corrosion-preventing effects.

[0017]

In particular, by using predetermined amounts of the copolymer (A) and the copolymer (B) and by maintaining the concentration of the zinc compound in the water system at a required concentration, it is possible to fully enhance the

corrosion-preventing effect in the non-phosphorus, zinc treatment even in a water system having high hardness under highly saline conditions.

Consequently, the present invention realizes an environmental load reduction treatment with an enhanced corrosion-preventing effect for a metal member in a cooling water system.

Brief Description of Drawings

[0018]

Fig. 1 is a flow diagram illustrating a testing apparatus used in Examples 1 and 2 and Comparative Examples 1 to 6.

Fig. 2 is a graph showing the results of Examples 1 and 2 and Comparative Examples 1 to 6.

Fig. 3 is a flow diagram illustrating a testing apparatus used in Examples 3 and 4 and Comparative Examples 7 and 8.

Detailed Description of Preferred Embodiments

[0019]

Embodiments of a method of preventing metal corrosion in a cooling water system according to the present invention will be described in detail below.

[0020]

In the present invention, by causing the following components (A), (B), and (C) to be present in a cooling

water system in which a non-phosphorus, zinc treatment is performed, corrosion of a metal member in the water system is inhibited:

(A) a copolymer of acrylic acid and a sulfone group-containing monomer (hereinafter described as the "copolymer (A)"),

(B) a copolymer of maleic acid and isobutylene (hereinafter described as the "copolymer (B)"), and

(C) a zinc compound.

[0021]

The copolymer (A) is a copolymer of acrylic acid and a sulfone group-containing monomer, and the sulfone group-containing monomer of the copolymer (A) is not particularly limited as long as it contains sulfone groups. As a preferable sulfone group-containing monomer, 2-acrylamide-2-methylpropanesulfonic acid and/or 3-allyloxy-2-hydroxypropanesulfonic acid may be mentioned.

[0022]

The molar ratio of acrylic acid to the sulfone group-containing monomer in the copolymer (A) is preferably 7:3 to 9:1 from the standpoint of obtaining the action of carboxyl groups of acrylic acid and the action of sulfone groups of the sulfone group-containing monomer in a well-balanced manner.

[0023]

When the molecular weight of the copolymer (A) is excessively small, the effect of inhibiting calcium carbonate scales decreases. When the molecular weight of the copolymer (A) is excessively large, gelation with calcium occurs. Therefore, the molecular weight of the copolymer (A) is preferably 500 to 50,000, and in particular, 5,000 to 20,000.

[0024]

As the copolymer (A), two or more types of copolymers having different molar ratios of acrylic acid to the sulfone group-containing monomer or different molecular weights may be used.

[0025]

On the other hand, the copolymer (B) is a copolymer of maleic acid and isobutylene, and the molar ratio of maleic acid to isobutylene in the copolymer (B) is preferably 5:5 to 8:2, and in particular, 1:1, from the standpoint of obtaining the action of carboxyl groups of maleic acid and the hydrophobic action of isobutylene in a well-balanced manner.

[0026]

When the molecular weight of the copolymer (B) is excessively small, the effect of inhibiting calcium carbonate scales decreases. When the molecular weight of the copolymer (B) is excessively large, gelation with

calcium occurs. Therefore, the molecular weight of the copolymer (B) is preferably 10,000 to 50,000, and in particular, 30,000 to 50,000.

[0027]

As the copolymer (B), two or more types of copolymers having different molar ratios of maleic acid to isobutylene or different molecular weights may be used.

[0028]

The zinc compound is not particularly limited, but one or two or more zinc compounds, such as zinc chloride and zinc sulfate, may be used.

[0029]

In the present invention, the amount of the copolymer (A) to be added to the water system is 3 to 25 mg-solid content/L relative to the blow water amount, and the amount of the copolymer (B) to be added to the water system is 3 to 25 mg-solid content/L relative to the blow water amount. The total amount of the copolymer (A) and the copolymer (B) to be added is preferably 5 to 50 mg-solid content/L relative to the blow water amount. Regarding the addition amount ratio of the copolymer (A) to the copolymer (B), in order to obtain the synergetic effect of the combined use thereof, the addition amount ratio by weight of the copolymer (A) to the copolymer (B) is preferably 1:0.5 to 1:2.

[0030]

Furthermore, preferably, the zinc compound is added at a zinc concentration of 0.5 mg/L or more, and in particular, about 0.5 to 3 mg/L, relative to the blow water amount of the water system.

[0031]

Note that the addition amount relative to the blow water amount is usually equal to the standard control concentration in the cooling water system.

[0032]

In the present invention, two or three of the copolymer (A), the copolymer (B), and the zinc compound may be mixed in advance and the resulting mixture may be added to the cooling water system, or each of these components may be added separately to the cooling water system. Although the point of addition is not particularly limited, addition is usually made to a cooling water tank in the cooling water system.

[0033]

In the method of preventing metal corrosion in a cooling water system of the present invention, a very excellent corrosion-preventing effect is obtained by combined use of the copolymer (A), the copolymer (B), and the zinc compound. Therefore, the corrosion-preventing effect is effectively exhibited even in a water system

having a high corrosion tendency, such as a water system having a high calcium hardness or a water system having a high concentration of corrosive ions. As the water quality of the cooling water system to which the present invention is applied, preferably, the calcium hardness is 100 to 1,000 mg-$CaCO_3$/L, and the concentration of corrosive ions (total of the concentration of chloride ions and the concentration of sulfate ions) is 2,000 mg/L or less.

Examples and Comparative Examples

[0034]

The present invention will be described more specifically on the basis of examples.

[0035]

In Examples and Comparative Examples below, the followings were used as the copolymer (A) and the copolymer (B):

<Copolymer (A)>

Copolymer of acrylic acid (AA) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS), molecular weight: 10,000, molar ratio of AA to AMPS: 8:2 (hereinafter abbreviated as "AA/AMPS")

Copolymer of acrylic acid (AA) and 3-allyloxy-2-hydroxypropanesulfonic acid (HAPS), molecular weight: 10,000, molar ratio of AA to HAPS: 8:2 (hereinafter abbreviated as "AA/HAPS")

<Copolymer (B)>

Copolymer of maleic acid (MA) and isobutylene (IB), molecular weight: 40,000, molar ratio of MA to IB: 1:1 (hereinafter abbreviated as "MA/IB")

As the zinc compound, zinc sulfate was used.

Furthermore, for comparison, a homopolymer of maleic acid (molecular weight: 500, hereinafter abbreviated as "MA") was used.

[Examples 1 and 2, Comparative Examples 1 to 6]

[0036]

Using a testing apparatus illustrated in Fig. 1, testing was performed in accordance with the procedure described below.

[0037]

A 5 wt% aqueous sodium bicarbonate solution was used in order to adjust the M-alkalinity, polymers shown in Table 1 were used, a 10 wt% aqueous calcium chloride solution was used in order to adjust the calcium hardness, a 10 wt% aqueous sodium chloride solution was used in order to adjust the chloride ion concentration, and an aqueous sodium sulfate solution was used in order to adjust the sulfate ion concentration. Furthermore, sulfuric acid was used for pH adjustment, and a 10 wt% aqueous zinc sulfate solution was used as the zinc compound solution. These components were added to pure water to prepare synthetic water having the

water quality described below.

[0038]

<Synthetic water quality>

M-alkalinity: 200 mg/L as $CaCO_3$

Polymer concentration: concentration shown in Table 1

Calcium hardness: 500 mg/L as $CaCO_3$

Chloride ion concentration: 500 mg/L

Sulfate ion concentration: 500 mg/L

Zinc concentration: 2 mg/L

pH: 8.6

[0039]

[Table 1]

	Polymer concentration (mg-solid content/L)				
	AA/AMPS	AA/HAPS	MA/IB	MA	Total
Example 1	3.75	-	1.25	-	5
Example 2	-	3.75	1.25	-	5
Comparative Example 1	1.25	3.75	-	-	5
Comparative Example 2	3.75	-	-	1.25	5
Comparative Example 3	-	3.75	-	1.25	5
Comparative Example 4	-	-	5	-	5
Comparative Example 5	5	-	-	-	5
Comparative Example 6	-	5	-	-	5

[0040]

The synthetic water was placed in a mother liquid tank 1, and the synthetic water in the mother liquid tank 1 was transferred to a test tank (retained water amount 50 L) 2. The synthetic water was circulated in the apparatus from the test tank 2 using a pump 3 at a flow rate of 0.5 m/sec, and the water was made to overflow such that the residence time was 80 hours. A carbon steel tube 4 and a corrosion sensor 5 were installed in the circulation system, and the corrosion rate (mdd) was measured with the corrosion sensor 5.

The test period was set at seven days.

The results are shown in Fig. 2.

[0041]

As is evident from Fig. 2, in the cooling water system having high hardness and high salinity, by combining the copolymer (A) with the copolymer (B), the corrosion rate at the time of combined use of zinc is significantly decreased, and a markedly excellent corrosion-preventing effect is obtained compared with the case where another polymer is used.

[Examples 3 and 4, Comparative Examples 6 and 7]

[0042]

Concentrated industrial water was produced using a testing apparatus illustrated in Fig. 3, and used as test water having the water quality shown in Table 2, and a test

was carried out.

In Fig. 3, reference numeral 11 designates a cooling tower, reference numeral 12 designates a cooling water tank, reference numerals 13A and 13B each designate a test piece column, reference numerals 14A and 14B each designate a heat exchanger, reference numerals 15A and 15B each designate an electric heater, reference numerals 16A and 16B each designate a heat-transfer tube, reference numerals P_1, P_2, and P_3 each designate a chemical feed pump, reference numeral P_4 designates a blow pump, and reference numeral P_5 designates a circulation pump. The cooling water in the cooling water tank 12 is circulated by the circulation pump P_5 into a circulating water system provided with the test piece columns 13A and 13B and into a circulating water system provided with the heat exchangers 14A and 14B. The circulating cooling water on the heat exchangers 14A and 14B side is cooled with the cooling tower 11, and then returned to the cooling water tank 12.

[0043]

[Table 2]

Water quality item		Control value
pH		9.0
Electrical conductivity	(mS/m)	200
Calcium hardness	(mg/L as $CaCO_3$)	400
M-alkalinity	(mg/L as $CaCO_3$)	350
Chloride ion concentration	(mg/L)	350
Sulfate ion concentration	(mg/L)	150

[0044]

Using the chemical feed pumps P_1 to P_3, the polymers shown in Table 3 were added into the cooling water tank 12 at the concentrations shown in Table 3, and an aqueous zinc sulfate solution was added such that the zinc concentration in the water system was 2 mg/L.

[0045]

Subsequently, the test water was circulated using the circulation pump P_5, and then thermal load was applied in the heat exchangers 14A and 14B. The test was carried out under the two conditions described below. Under each condition, the corrosion rate of the test pieces in the test piece columns 13A and 13B and the pitting corrosion depth in the heat-transfer tubes 16A and 16B after the test were measured. The test period was set at 14 days.

Condition I: flow rate 0.5 m/sec

ΔT = 10°C

(heat transfer amount = 46,000 kcal/m^2·hr)

Condition II: flow rate 0.25 m/sec

ΔT = 5°C

(heat transfer amount = 13,000 kcal/m^2·hr)

The flow rate means the flow rate of circulating cooling water flowing through the test piece columns 13A and 13B and the heat-transfer tubes 16A and 16B, and ΔT is the difference between the heat exchanger outlet temperature and the inlet temperature of circulating cooling water flowing through the heat-transfer tubes 16A and 16B.

[0046]

The results are shown in Table 4.

[0047]

[Table 3]

	Zinc concentration (mg/L)	Polymer concentration (mg-solid content/L)			
		AA/AMPS	AA/HAPS	MA/IB	Total
Examples 3 and 4	2.0	3	9	3	15
Comparative Examples 7 and 8	2.0	5.6	12.9	-	18.5

[0048]

[Table 4]

Test	Condition	Flow rate (0.5m/s)	Heat transfer amount ($Kcal/m^2 \cdot hr$)	Pitting corrosion depth (mm)	Corrosion rate (mdd)
Example 3	I	0.50	46000	0.15	3.3
Example 4	II	0.25	13000	0.16	4.1
Comparative Example 7	I	0.50	46000	0.34	20
Comparative Example 8	II	0.25	13000	0.34	26.7

[0049]

As is evident from Table 4, by adding the copolymer (A) and the copolymer (B) into a cooling water system in which a non-phosphorus, zinc treatment is performed, not only metal corrosion but also pitting corrosion can be effectively inhibited even under high hardness and high salinity conditions.

[0050]

1: mother liquid tank

2: test tank

3: circulation pump

4: carbon steel tube

5: corrosion sensor

11: cooling tower

12: cooling water tank

13A, 13B: test piece column

14A, 14B: heat exchanger

15A, 15B: electric heater

16A, 16B: heat-transfer tube

CLAIMS:

1. A method of preventing metal corrosion in a cooling water system, which is a method of preventing corrosion of a metal member in a cooling water system in which a non-phosphorus, zinc treatment is performed, the method comprising causing the following components (A), (B), and (C) to be present in the water system:

(A) a copolymer of acrylic acid and a sulfone group-containing monomer (hereinafter described as the "copolymer (A)"), wherein the sulfone group-containing monomer of the copolymer (A) is 2-acrylamide-2-methylpropanesulfonic acid and/or 3-allyloxy-2-hydroxypropanesulfonic acid,

(B) a copolymer of maleic acid and isobutylene (hereinafter described as the "copolymer (B)"), and

(C) a zinc compound.

2. The method of preventing metal corrosion in a cooling water system according to Claim 1, wherein the molecular weight of the copolymer (A) is 500 to 50,000, and the molar ratio of acrylic acid to the sulfone group-containing monomer is 7:3 to 9:1.

3. The method of preventing metal corrosion in a cooling water system according to any one of Claims 1 to 2, wherein the molecular weight of the

copolymer (B) is 10,000 to 50,000, and the molar ratio of maleic acid to isobutylene is 5:5 to 8:2.

4. The method of preventing metal corrosion in a cooling water system according to any one of Claims 1 to 3, wherein the zinc compound is zinc chloride and/or zinc sulfate.

5. The method of preventing metal corrosion in a cooling water system according to any one of Claims 1 to 4, wherein the copolymer (A) and the copolymer (B) are added in the amount of 5 to 50 mg-solid content/L in total relative to the blow water amount of the water system.

6. The method of preventing metal corrosion in a cooling water system according to any one of Claims 1 to 5, wherein the zinc compound is added in the amount of 0.5 mg/L or more relative to the blow water amount of the water system.

7. The method of preventing metal corrosion in a cooling water system according to any one of Claims 1 to 6, wherein the calcium hardness of the water system is 100 to 1,000 mg-$CaCo_3$/L, and the concentration of corrosive ions (total of the concentration of chloride ions and the concentration of sulphate ions) is 2,000 mg/L or less.