

AGENT FOR TREATING BOILER WATER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an agent for treating boiler water. More particularly, the present invention relates to an agent for treating boiler water which can provide steam having little smell and a small concentration of acetaldehyde and showing high safety although the agent contains a polymer derived from 2-acrylamido-2-methylpropanesulfonic acid.

2. Description of the Related Arts

When scale is formed in a boiler and attached to the surface of a pipe for supplying water disposed in the boiler and to the surrounding area, heat efficiency of the boiler decreases by the adverse effect on the heat conductivity. Moreover, portions to which scale is attached are locally overheated to decrease mechanical strength of the pipe and this occasionally leads to accidents such as swelling and rupture of the pipe. Therefore, various agents for suppressing scale formation and various agents for suppressing scale growth are added to boiler water in order to prevent problems caused by scale.

As the agent for suppressing scale formation or scale growth which does not contain phosphates and does not cause environmental pollution, polymers of a low molecular weight having carboxyl group are widely used. Polyacrylic acid is most widely used for this purpose. Various copolymers have been developed to increase the effect of preventing scale formation. For example, in Japanese Patent Application Laid-Open No. Showa

50(1975)-86489, a process comprising adding a copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid to suppress precipitation of salts forming scale is proposed.

The above copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid exhibits a larger effect of preventing scale formation than polyacrylic acid. However, when boiler water is treated with the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid, amines and acetaldehyde which is suspected to be a carcinogenic substance are formed by heat decomposition of the unit of 2-acrylamido-2-methylpropanesulfonic acid. Amines have low threshold values of smelling and the problem of smell occurs even when amines are present in low concentrations. Thus, an agent for treating boiler water which contains a polymer derived from 2-acrylamido-2-methylpropanesulfonic acid and does not cause the problems of generation of smell and formation of acetaldehyde in steam has been desired.

SUMMARY OF THE INVENTION

The present invention has an object to provide an agent for treating boiler water which can provide steam having little smell and a small concentration of acetaldehyde and showing high safety although the agent contains a polymer derived from 2-acrylamido-2-methylpropanesulfonic acid.

As the result of intensive studies by the present inventors to solve the above problems, it was found that, when a copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid is used in combination with an oxygen scavenger, the degree of smell and the

concentration of acetaldehyde can be decreased to the level obtained when polyacrylic acid alone is used. The present invention has been completed on the basis of this knowledge.

Accordingly, the present invention provides:

- (1) An agent for treating boiler water which comprises a copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and an oxygen scavenger; and
- (2) An agent for treating boiler water described in (1), wherein the copolymer has a molecular weight of 10,000 to 20,000.

Preferable embodiments of the present invention include:

- (3) An agent for treating boiler water described in (1), wherein the ratio by mol of units of (meth)acrylic acid to units of 2-acrylamido-2-methylpropanesulfonic acid, which are both constituting units of the copolymer, is 70/30 to 90/10;
- (4) An agent for treating boiler water described in (1), wherein the oxygen scavenger is a compound selected from the group consisting of a salt of sulfurous acid, succinic acid and a salt of succinic acid;
- (5) A process for treating boiler water comprising adding the agent for treating boiler water described in (1) to water in a boiler in such an amount that the concentration of the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid is 10 to 200 mg/liter; and
- (6) A process for treating boiler water comprising adding the agent for treating boiler water described in (1) to water supplied to a boiler in such an amount that the amount of the oxygen scavenger is equivalent to or more than the amount of oxygen dissolved in the water supplied to a boiler.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic diagram exhibiting a test apparatus used for simulating a boiler system in Examples.

- 1 A storage tank
- 2 A simulated boiler
- 3 A heat exchanger
- 4 A flow meter
- 5 A sampling valve

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The agent for treating boiler water of the present invention comprises a copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and an oxygen scavenger. (Meth)acrylic acid means either acrylic acid or methacrylic acid.

In the present invention, it is preferable that, in the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid, the ratio by mol of units of (meth)acrylic acid which constitute the copolymer to units of 2-acrylamido-2-methylpropanesulfonic acid which also constitute the copolymer is 70/30 to 90/10 and more preferably 75/25 to 85/15. When the ratio by mol of units of (meth)acrylic acid to units of 2-acrylamido-2-methylpropanesulfonic acid is less than 70/30, there is the possibility that amines and acetaldehyde are formed. When the ratio by mol of units of (meth)acrylic acid to units of 2-acrylamido-2-methylpropanesulfonic acid exceeds 90/10, there is the possibility that the effect of preventing scale formation in a boiler becomes insufficient.

In the present invention, it is preferable that the molecular weight

of the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropane-sulfonic acid is 10,000 to 20,000 and more preferably 13,000 to 20,000. When the molecular weight of the copolymer is less than 10,000, there is the possibility that amines and acetaldehyde are formed. When the molecular weight of the copolymer exceeds 20,000, there is the possibility that the effect of preventing scale formation in a boiler becomes insufficient.

It is preferable that the agent for treating boiler water of the present invention is added to water in a boiler in such an amount that the concentration of the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid is 10 to 200 mg/liter. When the concentration of the copolymer is less than 10 mg/liter, there is the possibility that the effect to prevent scale formation in a boiler becomes insufficient. When the concentration of the copolymer exceeds 200 mg/liter, there is the possibility that amines and acetaldehyde are formed.

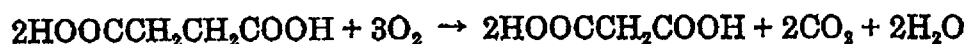
The oxygen scavenger used in the agent for treating boiler water of the present invention is not particularly limited. Examples of the oxygen scavenger include a salt of sulfurous acid, a salt of bisulfurous acid, a compound having two carboxyl groups and two or more methylene groups between the two carboxyl groups such as succinic acid, a salt thereof, hydrated hydrazine and hydrazine sulfate. Among these compounds, a salt of sulfurous acid, succinic acid and a salt of succinic acid are preferably used because there is no possibility that these compounds cause smell to steam.

It is preferable that the agent for treating boiler water of the present invention is added to water supplied to a boiler in such an amount that the

amount of the oxygen scavenger is equivalent to or more than the amount of oxygen dissolved in the water supplied to a boiler. For example, the reaction of sodium sulfite and oxygen takes place in accordance with the following equation:



Therefore, it is preferable that 8 mg/liter or more of sodium sulfite is added per 1 mg/liter of oxygen dissolved in water. The reaction of succinic acid and oxygen takes place in accordance with the following equation:



Therefore, it is preferable that 2.5 mg/liter or more of succinic acid is added per 1 mg/liter of oxygen dissolved in water.

The form of the agent for treating boiler water is not particularly limited. For example, the agent may be a single liquid agent in which the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and the oxygen scavenger are both dissolved. The agent may also be composed of two liquid parts which are a solution containing the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and a solution containing the oxygen scavenger. Alternatively, the agent may be composed of two powder parts which are powder of the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and powder of the oxygen scavenger. The agent may also be composed of one liquid part and one powder part, wherein either one of the copolymer and the oxygen scavenger is in the form of a solution and the other component is in the form of powder.

The agent for treating boiler water can be used in combination with other agents. The agents used in combination are not particularly limited

and other scale inhibitors and corrosion inhibitors can be used. Examples of the other scale inhibitor include polymers and copolymers of compounds such as (meth)acrylic acid, maleic acid, itaconic acid, hydroxyethyl methacrylate, acrylamide, vinylsulfonic acid, styrenesulfonic acid and 2-hydroxy-3-allyloxypropanesulfonic acid. Examples of the corrosion inhibitor include phosphates such as trisodium phosphate and disodium hydrogenphosphate and polyphosphates such as sodium hexameta-phosphate.

The boiler to which the agent for treating boiler water of the present invention is applied is not particularly limited. When the temperature of water exceeds 250°C, there is the possibility that the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid is decomposed. Therefore, it is preferable that the agent is applied to a low pressure boiler which is operated at a pressure of 3.0 MPa or less.

The mechanism according to which generation of smell and formation of acetaldehyde in steam can be suppressed by the agent for treating boiler water of the present invention is considered as follows. When oxygen is present in water in a condition of a high temperature and a high pressure, oxygen attacks a polymer to react with the polymer and a portion of the polymer is decomposed to form amines and acetaldehyde. Although the amount of amines formed is small, amines generally have low threshold values of smelling and tend to cause the problem of smell. The attack of oxygen to the polymer can be suppressed by the addition of the oxygen scavenger. When the molecular weight of the polymer is excessively small, the concentration of acetaldehyde increases because the ends of the polymer tend to be decomposed by the attacked by oxygen.

When the agent for treating boiler water of the present invention is used, an excellent effect of preventing scale formation can be exhibited by the effect of the copolymer containing 2-acrylamido-2-methylpropane-sulfonic acid and, at the same time, the degree of smell and the concentration of acetaldehyde can be kept at the same levels as those obtained by using polyacrylic acid. The agent for treating boiler water of the present invention can be particularly effectively used for decreasing smell in a system in which drain of steam is recovered.

To summarize the advantages obtained by the present invention, because the agent comprises the oxygen scavenger, the agent for treating boiler water of the present invention can provide steam having little smell and a small concentration of acetaldehyde and showing high safety although the agent contains the polymer derived from 2-acrylamido-2-methylpropanesulfonic acid.

EXAMPLES

The present invention is described more specifically with reference to examples. However, the present invention is not limited to the examples.

In Examples and Comparative Examples, the tests were conducted using the test apparatus for simulating a boiler system shown in Figure 1. The amount of recovery of drain in an actual boiler is generally 0 to 70%. However, the entire drain was recovered and recycled in this apparatus. The smell components and acetaldehyde formed by decomposition of the copolymer were not discharged to the outside but accumulated and concentrated in the system.

From a storage tank 1 having a volume of 20 liters, boiler water was transferred to a simulated boiler 2 at the flow speed of 5.55 liters/hr. The simulated boiler was operated at the pressure of 2.0 MPa and the amount of blow of 0.55 liters/hour. Formed steam is converted to drain in a heat exchanger 3 and the drain was returned to the storage tank through a flow meter 4 at a flow speed of 5.00 liters/hr. A sampling valve 5 is disposed at the piping for the drain and a portion of the drain was taken out as a sample. To the storage tank, water containing the agent for treating boiler water is added as the supplement at the speed of 0.55 liters/hr.

In Examples and Comparative Examples, the degree of smell and the concentration of acetaldehyde were measured in accordance with the following methods:

(1) Degree of smell

After a Tedlar® Bag having a volume of 5 liters was filled with dry air, 0.5 ml of drain was injected into the pack using a syringe. The hole made by the syringe was closed with a tape and the pack was left standing at room temperature for 3 days. After it was confirmed that the drain had completely vaporized, the degree of smell was evaluated by the organoleptic test.

(2) Concentration of acetaldehyde

The concentration of acetaldehyde was measured in accordance with the head space GC-MS method using CD₃CDO.

Example 1

To softened water having the concentration of dissolved oxygen of 6 mg/liter, 100 mg/liter of a copolymer of acrylic acid and 2-acrylamido-2-

methylpropanesulfonic acid (ratio by mol, 80/20; molecular weight, 13,000), 60 mg/liter of sodium sulfite and 10 mg/liter of sodium hydroxide were added to prepare test water and a test run was conducted using the prepared test water.

A sample was taken out from drain after a continuous operation for 40 hours and the degree of smell and the concentration of acetaldehyde were measured. The degree of smell was 32 and no acetaldehyde was detected.

Example 2

A test run was conducted in accordance with the same procedures as those conducted in Example 1 except that a copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 70/30; molecular weight, 13,000) was used in place of the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 80/20; molecular weight, 13,000). The degree of smell was 250 and no acetaldehyde was detected.

Example 3

A test run was conducted in accordance with the same procedures as those conducted in Example 1 except that a copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 60/40; molecular weight, 13,000) was used in place of the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 80/20; molecular weight, 13,000). The degree of smell was 800. Slight smell was felt in the drain but the degree of the smell was not in the range causing any

problem. No acetaldehyde was detected.

Comparative Example 1

A test run was conducted using test water to which sodium sulfite was not added. Specifically, to softened water having the concentration of dissolved oxygen of 6 mg/liter, 100 mg/liter of a copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 80/20; molecular weight, 13,000) and 10 mg/liter of sodium hydroxide were added to prepare test water and a test run was conducted using the prepared test water in accordance with the same procedures as those conducted in Example 1.

A sample was taken out from drain after a continuous operation for 40 hours and the degree of smell and the concentration of acetaldehyde were measured. The degree of smell was 5,500 and the concentration of acetaldehyde was 6.0 mg/liter.

The results of Examples 1 to 3 and Comparative Example 1 are shown in Table 1.

Table 1

	copolymer ¹⁾		sodium	sodium	degree of	concn. of
	amount (mg/liter)	AMPS ²⁾ (% by mol)	sulfite (mg/liter)	hydroxide (mg/liter)	smell	acetaldehyde (mg/liter)
Example 1	100	20	60	10	32	not detected
Example 2	100	80	60	10	250	not detected
Example 3	100	40	60	10	800	not detected
Comparative Example 1	100	20	0	10	5500	6.0

1) A copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid

2) 2-Acrylamido-2-methylpropanesulfonic acid

As shown by the results in Table 1, the degree of smell in drain was low and no acetaldehyde was detected in Examples 1 to 3 in which the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and sodium sulfite were added. Thus, it was shown that steam having a high level of safety was supplied. When the content of the unit of 2-acrylamido-2-methylpropanesulfonic acid in the copolymer is in the range of 20 to 40% by mol, the smaller the content of the unit of 2-acrylamido-2-methylpropanesulfonic acid, the lower the degree of smell. In contrast, in Comparative Example 1 in which the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid alone was added and sodium sulfite was not added, the degree of smell and the concentration of acetaldehyde were both large and it was shown that impurities were contained in the steam.

Example 4

The effect of the molecular weight of the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid on the concentration of acetaldehyde in drain was examined.

Into pure water having the concentration of dissolved oxygen of 7.5 to 8.5 mg/liter, 1,000 mg/liter of a copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid (ratio by mol, 80/20), 200 mg/liter of sodium sulfite, 74 mg/liter of sodium sulfate and 82 mg/liter of sodium chloride were dissolved. The prepared solution in an amount of one liter was adjusted to a pH of 11.8 with sodium hydroxide and transferred to a 1.5 liter autoclave. The autoclave was closed, heated and kept at 213°C (a pressure of 2.0 MPa) for 24 hours. Then, 50 ml of a sample was taken out and the concentration of acetaldehyde in the sample was measured.

When the molecular weight of the copolymer was 3,000, the concentration of acetaldehyde was 35 mg/liter. When the molecular weight of the copolymer was 8,200, the concentration of acetaldehyde was 2.8 mg/liter. When the molecular weight of the copolymer was 9,700, the concentration of acetaldehyde was 0.5 mg/liter. When the molecular weight of the copolymer was 12,000, 13,000 and 14,000, the concentration of acetaldehyde was 0.1 mg/liter or lower in all cases.

The results obtained in Example 4 are shown in Table 2.

Table 2

molecular weight	concentration of acetaldehyde
3000	35
8200	2.8
9700	0.5
12000	<0.1
13000	<0.1
14000	<0.1

As shown by the results in Table 2, the larger the molecular weight of the copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid, the larger the effect to decrease the concentration of acetaldehyde. When the molecular weight exceeds 10,000, the concentration of acetaldehyde decreased to hardly detectable levels.



CLAIMS:

1. An agent for treating boiler water which comprises a copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid and an oxygen scavenger.
2. An agent for treating boiler water according to Claim 1, wherein the copolymer has a molecular weight of 10,000 to 20,000.
3. An agent for treating boiler water according to Claim 1, wherein the ratio by mol of units of (meth)acrylic acid to units of 2-acrylamido-2-methylpropanesulfonic acid, which are both constituting units of the copolymer, is 70/30 to 90/10.
4. An agent for treating boiler water according to Claim 1, wherein the oxygen scavenger is a compound selected from the group consisting of a salt of sulfurous acid, succinic acid and a salt of succinic acid.
5. A process for treating boiler water comprising adding the agent for treating boiler water described in Claim 1 to water in a boiler in such an amount that the concentration of the copolymer of (meth)acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid is 10 to 200 mg/liter.
6. A process for treating boiler water comprising adding the agent for treating boiler water described in Claim 1 to water supplied to a boiler in such an amount that the amount of the oxygen scavenger is equivalent to



or more than the amount of oxygen dissolved in the water supplied to a boiler.