

SPECIFICATION

ANTI-CORROSIVE AGENT FOR BOILERS

5 TECHNICAL FIELD

[0001] The present invention relates to an agent for treating boiler water, more specifically to an anti-corrosive agent that is suitably used for boiler plants including mainly a boiler that is equipped with a superheater or a steam turbine and a boiler whose treated water is mixed with a boiler that is equipped with a superheater or a steam turbine.

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BACKGROUND ART

[0002] A boiler is structured to heat boiler water at high temperature and generate steam.

An anti-corrosive agent is used to prevent corrosion of metal that forms the boiler. In particular, for a boiler that is equipped with a superheater or a steam turbine, such as an

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electrical power generator boiler and an incinerator boiler, ion-exchanged water or demineralized water is mainly used as make-up water. Thus, in many cases, these boilers are operated at a concentration rate, which is a water quality control item, from about 30 times to about 200 times. In these boilers, caustic alkali is not used, but phosphate is added to control the pH of boiler water and to prevent corrosion. A neutralizing amine or ammonia is also

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added to increase the pH of condensate and feed water and to prevent iron dissolution.

Whereby, the amount of iron that is brought into a boiler can is reduced.

[0003] However, in recent years, a trouble of lowering the pH of boiler can water has been frequently occurred. The trouble is caused by: the fact that source waters are diversified and water quality is degraded, so that the amount of organic substances that are brought into the boiler can is increased; reduction of blow quantity for aiming at saving energy and water; and application of an organic deoxidizer free of hydrazine. As a countermeasure thereof, in some cases, phosphate concentration in boiler water is increased or a phosphate-based boiler compound having a Na/PO₄ mole ratio of more than 3 is used. However, in this case, occurrence of phosphate hide-out phenomena or alkali corrosion is concerned about.

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As a typical anti-corrosive agent for condensate and feed water that is used in the above system, 2-aminoethanol (MEA) may be mentioned. However, an effect of elevating the pH of boiler water is not sufficient. Further, as an alternative, Patent Document 1 discloses methyldiethanolamine (MDEA).

When MDEA described in Patent Document 1 is used as an anti-corrosive agent, in a little amount of the agent, the pH is easily elevated in a high-temperature corrosive environment. In addition, volatility thereof is low, so that carrying over to vapor is reduced and that influence to reaction system is small. Furthermore, when a deoxidizer is used in combination, deoxidizing ability is allowed to be enhanced. In this way, with a small amount of addition, a high anti-corrosion effect is described to be expected.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004] Patent Document 1: Japanese Patent Laid-Open Publication No. 2003-231980

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] However, a preferred amount of addition to feed water of the anti-corrosive agent of MDEA described in Patent Document 1 is from 50 mg/L to 200 mg/L (paragraph [0012]). Accordingly, an anti-corrosive agent that is effective even in still smaller amount of addition has been expected.

The present invention has been performed as a result of extensive studies in order to solve the aforementioned problems. An object of the present invention is to provide an agent that is capable of keeping the pH of boiler water more effectively and preventing not only the inside of a boiler can but also entire boiler system including condensate and feed water from being corroded in the aforementioned boilers, while much more phosphate is not added and the Na/PO₄ mole ratio is not increased higher than 3.0.

MEANS FOR SOLVING THE PROBLEMS

[0006] Namely, the present invention provides following items of (1) to (4).

(1) An anti-corrosive agent for boilers, which includes therein diethanolamine.

(2) An anti-corrosive agent for boilers, which includes therein diethanolamine and a deoxidizer.

(3) An anti-corrosive agent as described in (2), wherein the deoxidizer is at least one kind of compounds selected from a group consisting of hydrazine, carbohydrazide, 1-aminopyrrolidine, 1-amino-4-methylpiperazine, N, N-diethylhydroxylamine, erythrobic acid and a salt thereof, and ascorbic acid and a salt thereof.

(4) An anti-corrosive agent as described in any of (1) to (3), wherein a neutralizing amine and/or ammonia is further added therein.

EFFECT OF THE INVENTION

5 [0007] The anti-corrosive agent for boilers according to the present invention keeps efficiently the pH of boiler water and prevents effectively not only the inside of a boiler can but also entire boiler system including condensate and feed water from being corroded, while much more phosphate is not added and the Na/PO₄ mole ratio is not increased higher than 3.0.

10 MODE FOR CARRYING OUT THE INVENTION

[0008] The anti-corrosion agent according to the present invention is characterized by including therein diethanolamine (hereinafter, called as “DEA” in some cases).

Diethanolamine is a compound that is represented by HOCH₂CH₂NHCH₂CH₂OH, which is an amine having low volatility, high thermal stability, and high dissociation degree,
15 whereby diethanolamine is carried over in a small amount to the side of vapor generated in a boiler, stays in boiler water, and provides a high ability of keeping the pH of boiler water.

Owing to that, diethanolamine may be used solely as an anti-corrosive agent. Further, diethanolamine may be used in combination with the other volatile amines, for example, amines having a high volatility, whereby the amount of amines carried over to the
20 vapor may be regulated and entire boiler system including the pH of condensate and feed water is prevented from being corroded. Furthermore, an additional anti-corrosive agent, a film-forming anti-corrosive agent that adsorbs to metal surface and forms films, a stabilizer, and the other auxiliary agent may be used in combination.

[0009] In the present invention, an anti-corrosive agent that uses diethanolamine and a
25 deoxidizer in combination is preferable. Known deoxidizers may be used, but a preferable deoxidizer is at least one kind of compounds selected from a group consisting of hydrazine, carbohydrazide, hydroquinone, 1-aminopyrrolidine, 1-amino-4-methylpiperazine, N, N-diethylhydroxylamine, isopropylhydroxylamine, erythroic acid and a salt thereof, and ascorbic acid and a salt thereof. A more preferable one is 1-amino-4-methylpiperazine
30 (hereinafter, called as “1A4MP” in some cases).

In addition, when an organic deoxidizer of non-hydrazines is used in combination, it may be added in a sufficient amount without lowering the pH of boilers.

As mentioned above, the present invention is resistant against incursion of organic

substances, and concentration-up of boilers is allowed to be performed.

[0010] The anti-corrosive agent that includes therein diethanolamine or diethanolamine and a deoxidizer in combination may be the one that includes only these components. In addition to that, water or the other solvent or the other components may be further included in combination. In the case of combination, each component may be separately introduced and combined together in boilers, or may be preliminary combined together and then introduced into boilers.

[0011] In the present invention, diethanolamine (DEA) is added to feed water in an amount of generally from 0.01 mg/L to 100 mg/L, preferably from 0.05 mg/L to 50 mg/L, and more preferably from 0.1 mg/L to 10 mg/L.

The anti-corrosive agent according to the present invention may be used in combination with at least one kind selected from ammonia and a neutralizing amine so as to prevent condensate system from being corroded.

The neutralizing amine vaporizes along with steam that is generated in a boiler, and dissolves in condensate at the same time when the vapor is condensed. Carbon dioxide in the steam condensate system is neutralized and the pH of the steam condensate is increased, whereby steel is prevented from being corroded. Ammonia has a similar effect to the neutralizing amine.

Preferable examples of the neutralizing amine include: monoethanolamine (MEA); cyclohexylamine (CHA); morpholine (MOR); diethylethanolamine (DEEA); monoisopropanolamine (MIPA), 3-methoxypropylamine (MOPA), and 2-amino-2-methyl-1-propanol (AMP). Among these, 3-methoxypropylamine (MOPA) is more preferable.

The ratio of these neutralizing amines and/or ammonia to diethanolamine (DEA), that is, DEA:[neutralizing amines and/or ammonia] (mass ratio), is preferably from 0.01:100 to 100:0.01, more preferably from 0.01:10 to 10:0.01, and still more preferably from 0.1:10 to 10:0.1.

[0012] In addition, the anti-corrosive agent for boilers according to the present invention includes therein preferably diethanolamine and a deoxidizer. Regarding the addition amount of the deoxidizer, necessary amount is added in accordance with the amount of dissolved oxygen in feed water. When a deaeration unit is involved, the deoxidizer is added in accordance with the performance of the deaeration unit.

Note that, when an anti-corrosive agent includes therein diethanolamine and a deoxidizer, the blending ratios of these two are selected as: diethanolamine is blended in a

ratio required to adjust at a predetermined pH of boiler water, generally in a range of from 8.8 to 10.8; and the deoxidizer is blended in a ratio sufficient to remove dissolved oxygen in feed water at that pH. Specifically, generally, diethanolamine may be blended in a ratio from 0.1% by mass to 99.9% by mass, preferably from 0.5% by mass to 95% by mass, and more preferably from 1% by mass to 90% by mass. The deoxidizer may be blended in a ratio from 99.9% by mass to 0.1% by mass, preferably from 99.5% by mass to 5% by mass, and more preferably from 99% by mass to 10% by mass.

The addition amount of the other anti-corrosive agents and the other agents may be determined appropriately within the range of purpose thereof. The blending ratios of water and the other solvents may be determined appropriately, but they may not be contained at all or may be contained within a range where moisture is allowed to be absorbed in accordance with the moisture-absorption properties of the agents themselves.

[0013] Boilers to which the anti-corrosive agent according to the present invention is applied are not particularly limited, but the anti-corrosive agent is particularly suitably applied to (1) a boiler that is equipped with a superheater and a steam turbine, (2) a boiler whose condensate and feed water is mixed with a boiler that is equipped with a superheater and a steam turbine, and the like.

[0014] The anti-corrosive agent according to the present invention exerts anticorrosion effect thereof in a condition where the anti-corrosive agent is added in boiler water of the aforementioned boilers. In a preferred method of addition, the anti-corrosive agent is added in feed water system, and, along with the feed water, the anti-corrosive agent runs into a boiler and is mixed with boiler water. However, direct addition to the boiler water may be performed. In the boiler, a part of diethanolamine (DEA) vaporizes and is taken out along with vapor, and the deoxidizer is consumed by deoxidizing action. Accordingly, a given amount of addition to the feed water allows the concentration of the anti-corrosive agent in the boiler water to be kept constant.

EXAMPLES

[0015] The present invention is further described in detail with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

EXAMPLE 1

(1) An anticorrosion test was performed by using a test boiler under the conditions: 4

MPa of pressure; 1% of blow rate; 20% of condensate recovery; feeding pure water (ion-exchanged water); and using a heating deaeration unit having an exit deaeration ability (amount of dissolved oxygen: DO value) of 0.03 mg/L. Note that, in this example, sodium phosphate was added at a Na/PO₄ mole ratio of 2.7 in an amount of 0.1 mg/L in terms of phosphate ion to feed water, and 2-aminoethanol (MEA) was added in an amount of 1 mg/L to feed water, whereby the pH of condensate and feed water became 9.1 and the pH of boiler water became 10.0. Here, assuming that an organic acid was produced in boiler water by thermal decomposition of organic substances that were derived from make-up water, formic acid was added in an amount of 0.06 mg/L to feed water. On this occasion, the pH (25°C) of boiler water lowered to 9.0, which fell below 9.4 that was the lower limit of JIS reference value for a boiler of this pressure rating.

While the amount of the agent added was not changed, in place of MEA, methyldiethanolamine (MDEA) was added in an amount of 1 mg/L. The pH (25°C) of boiler water was unchanged to be 9.0.

(2) On this occasion, when MDEA was switched to diethanolamine (DEA), the pH of boiler water elevated to 9.4, which went over the JIS reference value.

As mentioned above, it was known that diethanolamine (DEA) elevates more easily the pH of boiler water even in an equal amount of addition.

[0016] EXAMPLE 2

(1) An anticorrosion test was performed by using a test boiler under the conditions: 4 MPa of pressure; 1% of blow rate; 20% of condensate recovery; feeding pure water (ion-exchanged water); and using a heating deaeration unit having an exit deaeration ability (DO value) of 0.03 mg/L. In this example, to feed water, sodium phosphate was added at a Na/PO₄ mole ratio of 2.7 in an amount of 0.1 mg/L in terms of phosphate ion, formic acid was added in an amount of 0.1 mg/L as an organic acid that was produced in boiler water by thermal decomposition of organic substances that were derived from make-up water, and 2-aminoethanol (MEA) was added in an amount of 4 mg/L. The pH (25°C) of boiler water indicated 9.4 and the pH (25°C) of concentrate and feed water indicated 9.6. That is, the pH of concentrate and feed water increased more than needed. Here, in place of MEA, methyldiethanolamine (MDEA) was used. The amount of MDEA added was increased to 4.3 mg/L in order to keep the pH (25°C) of boiler water at 9.4. Furthermore, in place of MDEA, MIPA was used. The amount of MIPA added was increased to 7.1 mg/L in order to keep the pH (25°C) of boiler water at 9.4.

(2) Here, monoisopropanolamine (MIPA) was switched to diethanolamine (DEA). Similarly, in order to keep the pH (25°C) at 9.4, the amount of DEA added was reduced to 2.5 mg/L. At this time, the pH (25°C) of condensate and feed water lowered to 9.1, so that MEA was added additionally in an amount of 0.8 mg/L. Whereby, the total amount of chemicals added was reduced to 3.3 mg/L, and the pH (25°C) of boiler water indicated 9.5 and the pH (25°C) of concentrate and feed water indicated 9.3. Accordingly, a treatment that satisfied the JIS standard was allowed to be performed.

Similarly, to 2.5 mg/L diethanolamine (DEA), MIPA was added additionally in an amount of 1.4 mg/L. The total amount of chemicals added was reduced to 3.9 mg/L as compared with the case where MIPA or MEA was used solely. In addition to that, the pH (25°C) of boiler water indicated 9.4 and the pH (25°C) of concentrate and feed water indicated 9.3. Accordingly, a treatment that satisfied the JIS standard was allowed to be performed.

[0017] EXAMPLE 3

An anticorrosion test was performed, with respect to a system that included diethanolamine (DEA) and a deoxidizer of 1-amino-4-methylpiperazine (1A4MP) and a system of methyldiethanolamine (MDEA), by using a test boiler under the conditions: 4 MPa of pressure; 1% of blow rate; 20% of condensate recovery; feeding pure water (ion-exchanged water); and using a heating deaeration unit having an exit deaeration ability (DO value) of 0.03 mg/L. Test conditions and results are shown in Table 1.

[0018] Table 1

Test No.	Test conditions	pH of boiler water (25°C)	pH of condensate and feed water (25°C)	Total iron concentration (mg/L)
1	DEA(3.3 mg/L)	9.6	9.2	0.08 ⁵
2	DEA(3.3 mg/L) + 1A4MP(0.2 mg/L)	9.6	9.2	0.03
3	DEA(2.5 mg/L) + 1A4MP(0.2 mg/L) + MEA(0.8 mg/L)	9.5	9.3	0.01
4	DEA(2.5 mg/L) + 1A4MP(0.2 mg/L) + MIPA(0.8 mg/L)	9.5	9.3	0.01 ¹⁰
5	MDEA (3.3 mg/L)	8.8	9.2	1.1

15 [0019] Table 1 shows that the pH (25°C) of boiler water is as low as 8.8, so that the effect of reducing iron concentration is insufficient in test No. 5 where only methyldiethanolamine (MDEA) is used.

As opposed to this, the effect of reducing iron concentration is shown to be improved in test No. 1 where MDEA is replaced by diethanolamine (DEA).

20 In test No. 2 where DEA and a deoxidizer of 1A4MP are used in combination, the effect of reducing iron concentration is shown to be still more improved.

Furthermore, when test No. 1 and No. 2 are compared with test No. 3 and No. 4, it is shown that, even though the amount of DEA added is small, the effect of reducing iron concentration is enhanced by using in combination DEA and the other amines, that is, 2-aminoethanol (MEA) in test No. 3 and monoisopropanolamine (MIPA) in test No. 4.

INDUSTRIAL APPLICABILITY

[0020] The anti-corrosive agent according to the present invention is preferably used mainly in a boiler that is equipped with a super heater or a steam turbine, a boiler whose treated water is mixed with a boiler that is equipped with a super heater or a steam turbine, and the like.

CLAIMS

1. An anti-corrosive agent for boilers, comprising diethanolamine.
- 5 2. An anti-corrosive agent for boilers, comprising:
diethanolamine and
a deoxidizer.
3. The anti-corrosive agent according to claim 2, wherein
10 the deoxidizer is at least one kind of compounds selected from a group consisting of
hydrazine, carbohydrazide, 1-aminopyrrolidine, 1-amino-4-methylpiperazine, N, N-
diethylhydroxylamine, erythrobic acid and a salt thereof, and ascorbic acid and a salt thereof.
4. The anti-corrosive agent according to any one of claims 1 to 3, wherein
15 at least one kind selected from ammonia and a neutralizing amine is additionally
added.