

## DESCRIPTION

## METHOD OF CORROSION PREVENTION FOR RESTING BOILER

## 5 TECHNICAL FIELD

[0001]

The present invention is related to corrosion prevention method of a boiler during shutdown, in particular a corrosion prevention method of a boiler which is filled with water including chemicals and stored.

10

## BACKGROUND ART

[0002]

When a boiler plant is shut down, the temperature of a boiler water decreases, and the pressure becomes negative which is lower than air pressure to absorb external air which includes oxygen leading to a cause of corrosion. Thus, in the case where a boiler is shut down for a relatively long period of time (for example, more than one week), there is a need to prevent corrosion of the boiler during shut down.

[0003]

20 Conventionally, a method in which a boiler water is completely blown and a boiler drum is dried using a desiccant such as silica gel which is placed inside the boiler drum, and a dry storage method in which the boiler drum is sealed with a nitrogen gas, have been adopted as methods to prevent corrosion of a boiler plant during shut down  
25 (Japan Industrial Standard JIS B8223 established 1999).

[0004]

However, in the case where the boiler water can not be discharged or the boiler water can not be completely blown because the structure of the boiler itself is complex, it becomes difficult to adopt the  
30 above mentioned dry storage method and thus a wet storage method is

adopted instead (JIS B8223 established 1999).

[0005]

In this method, water obtained by adding either hydrazine at an additive amount of 100 to 1000 mg/Liter or sodium nitrite at an additive  
5 amount of 200 to 500 mg/Liter to pure water or soft water is used as water for storage (storage water), and a boiler drum is filled with the storage water and stored.

[0006]

In recent years, as an alternative to these wet storage methods  
10 mentioned above, a method in which an amine with neutralizing property such as monoethanolamine, monoisopropanolamine, cyclohexylamine, 2-amino-2-methyl-1-propanol, or morpholine is added at an additive amount of 100 to 1000 mg/Liter has been proposed (Japanese Laid Open Patent Publication No.2002-129366).

15 [0007]

However, these conventional methods have problems such as the following.

[0008]

That is, according to the dry storage method, when the shut down  
20 period is over a long period of time the desiccant must be periodically replaced and is therefore troublesome.

[0009]

Because hydrazine is suspected to have a carcinogenicity, its use may be avoided. In addition, because sodium nitrite is a solid  
25 compound, in a boiler which includes a superheater or a turbine, sodium nitrite can only be applied in the case where it can be back washed with pure water after storage.

[0010]

Although problems such as the above mentioned problems have  
30 been solved by the wet storage method which uses storage water which

includes the amine with neutralizing property, the following problems still remain in, for example, a boiler which is operated with a high pressure or high temperature superheater. That is, when the amine with neutralizing property is mixed with operating water (water which exists inside the drum of a boiler and is heated to generate steam during the boiler is operated), organic acid or carbon dioxide is produced by thermal decomposition of the amine to decrease the pH of feed water, condensate, or boiler water, or to increase acid conductivity of feed water or steam, and it is feared that the boiler operation will be troubled, though it depends on a recovery ratio of condensate. As a result, a problem arises in which it is necessary to blow all the storage water, and yet, in the case where there are spaces from which water cannot be discharged, it is also necessary to sufficiently clean the inside of the drum using pure water when the operation is started again. In addition, although some kinds of amine with neutralizing property are permitted to be used as a boiler additive under United States Food and Drug Administration (FDA) standards, they are not approved as a food additive in Japan. As a result, in the case where the steam which is produced from a boiler comes into direct contact with human or food products, users tends to be unwilling to use the amine because of safety.

## DISCLOSURE OF THE INVENTION

### PROBLEMS TO BE SOLVED

[0011]

The object of the present invention is to propose a method of corrosion prevention for a resting boiler, which can be applied to any boiler and by which a high level of safety towards humans and high corrosion prevention effects over a long period of time can be obtained.

## MEANS FOR SOLVING THE PROBLEMS

[0012]

The present invention proposes the following method of corrosion prevention for a resting boiler.

- 5 (1) A method of corrosion prevention for a resting boiler comprising:  
shutting down a boiler which is operated, said boiler being  
supplied with dehardnees water; and then,  
filling a drum of said boiler with a storage water which is obtained  
by adding ammonia to dehardness water, and storing.
- 10 (2) The method of corrosion prevention for a resting boiler according  
to (1), wherein said dehardness water is a pure water,  
supplying water which is obtained by adding ammonia to a boiler  
water, said boiler water being held in said boiler drum, to the inside of  
said boiler drum as said storage water.
- 15 (3) The method of corrosion prevention for a resting boiler according  
to (1), wherein  
discharging a boiler water from the inside of said boiler drum;  
and then,  
supplying a water which is obtained by adding ammonia to  
20 dehardness water to the inside of said boiler drum as said storage  
water.
- (4) The method of corrosion prevention for a resting boiler according  
to any one of (1) to (3), wherein said boiler is made from steel.
- (5) The method of corrosion prevention for a resting boiler according  
25 to (4), wherein said boiler has a superheater and is operated with a  
recovery ratio of 50% or more.

## EFFECTS OF THE INVENTION

[0013]

- 30 As above, according to the present invention, because corrosion

of a boiler during shutdown can be easily prevented by a method in which the boiler is filled with an ammonia solution, the corrosion prevention method of the present invention can be applied to any type of boiler. For example, the present invention can prevent corrosion of  
5 boilers to which the dry storage cannot be applied or boilers to which the wet filling storage which uses a solid corrosion prevention material such as sodium nitrite cannot be applied. Furthermore, even in the case where a boiler is shut down for a long period of time and stored, when the boiler corrosion prevention method of the present invention is  
10 applied, high corrosion prevention effects are preserved.

[0014]

In addition, because the ammonia does not contain carbon, even if the storage water is not completely blown or the boiler drum is not sufficiently washed after storage, it is possible to avoid causing a  
15 decrease in the pH of feed water, condensate, or boiler water because organic acid and carbon dioxide etc. are produced as pyrolysates after the operation of the boiler is started again. As a result, it is possible to avoid hindering the boiler operations due to an increase in acid conductivity of feed water or steam. According to the present invention,  
20 it is possible to obtain favorable drum storage effects with an even smaller amount of additives for preparing storage water compared to the method using the amine with neutralizing property.

[0015]

Furthermore, the ammonia which is used in this invention is cited  
25 as a DIRECT FOOD SUBSTANCE under United States FDA standards and is also recognized as a food additive in Japan having a high level of safety for humans. As a result, after a boiler is shut down, even if all the storage water is not blown even after the operation of the boiler is started again, the boiler water which is obtained after resumption of  
30 boiler operations has a low possibility of containing harmful substances

for humans.

## EMBODIMENT FOR CARRYING OUT THE INVENTION

[0016]

5 Dehardness water in the present invention means water which has undergone a treatment in which the hard components are removed and soft water and pure water belong to the category of the dehardness water. Soft water means water which has undergone a demineralizing treatment, specifically, it is preferred that concentrations of each of Ca  
10 and Mg which are hard components be 1 mg  $\text{CaCO}_3$ /Liter or less. Pure water is water in which impurities within water have been removed by filtration or a demineralizing treatment, that is, in which impurities other than the hard components, such as ions other than the hard components, organic substances, and the like, have been removed.

15 [0017]

The corrosion prevention method of the present invention can be applied to any boiler, more specifically, a cylindrical boiler, a water tube boiler, a through flow boiler and a circulation boiler and the like. These boilers may also be low pressure boilers, medium pressure boilers, or  
20 high pressure boilers. In addition, the corrosion prevention method of the present invention can also be applied to a boiler having a superheater or a turbine which cannot be back washed.

[0018]

A pure water boiler or a soft water boiler in which pure water or  
25 soft water is supplied for boiler operation is suitable as boilers for use with the present invention.

[0019]

The corrosion prevention method of the present invention is carried out in these types of boilers depending on the differences of raw  
30 water in the following way.

[0020]

First, in the case of a pure water boiler, after the boiler is shut down, the boiler is filled with storage water which has been added with ammonia. Because steam is constantly produced during operation of the boiler, the surface of the boiler water (operating water) which is inside the boiler drum is near the normal water level and the remaining upper space of the boiler drum consists of vapor. Then, the boiler is filled by adding water (feed water) which is further supplied to the boiler and at this time storage water which has been prepared by adding ammonia to the feed water is supplied.

[0021]

In this way, after the drum of the boiler is filled with water, the boiler is protected from corrosion during shut down by being stored in this state.

[0022]

Next, in the case of a soft water boiler, after the boiler is shut down the boiler water inside the boiler drum is once blown. In the case of feeding soft water, the soft water contains a variety of condensed components because the soft water (boiler water) which has been supplied to the boiler drum is condensed during operation of the boiler. As a result, if the boiler is shut down while the boiler water is still in the boiler drum, it is likely to be a cause of boiler corrosion. Therefore, the boiler water is once blown. Furthermore, while it is preferred that the boiler water be completely blown, in the case where the boiler water can not be completely blown, a blowing procedure is preferred in which the boiler water is discharged as much as possible and then remaining boiler water is replaced by supply water.

[0023]

Even in the case of the above stated feeding pure water, it may be necessary to blow the boiler water in the same way according to the

quality of the boiler water or condition of the equipment. The following case is an example of a case where the boiler water is blown even when pure water is supplied. In this case, a phosphate or alkali hydroxide is used as a boiler compound and it is feared that boiler water may enter  
5 into a super heater etc. when the boiler is filled

[0024]

Next, soft water or pure water which has been added with ammonia is supplied to the empty boiler until it is full.

[0025]

10 In either case, it is necessary to adjust the concentration of the added ammonia depending on water quality or storage period of time, however, generally it should be 10 to 500 mg/Liter, preferably 20 to 300 mg/Liter or more preferably about 30 to 100 mg/Liter.

[0026]

15 As a result of introducing ammonia, carbon dioxide or other acidic substances which exists within the boiler are neutralized, the pH level of the water (storage water) inside the boiler drum is increased and the storage water is maintained to be alkaline. As a result, boiler corrosion can be prevented over a long period of time.

20 [0027]

The above stated corrosion prevention effects are obtained by an ammonia additive concentration of 10 mg/Liter or more, and the more the additive concentration is increased the greater the corrosion prevention effects, however, when economies are considered it is  
25 preferred that the concentration have an upper limit of about 500 mg/Liter or more preferably 300 mg/Liter when odor is considered.

[0028]

The pH of the water which has been added with ammonia should be 9.5 or more, or more preferably, 10 or more. Depending on the  
30 setting conditions, phosphate or alkali hydroxide or the like which are

generally used as boiler compounds may be used in combination.

[0029]

The ammonia may be directly added to each feed water as an ammonia gas or as an ammonia water.

5 [0030]

The ammonia is cited as a DIRECT FOOD SUBSTANCE of FDA standards and is also a compound recognized as a food additive in Japan having a high level of safety with the above stated concentration.

[0031]

10 It is preferred that the boiler to be used with the present invention be made from steel for the reason that there are no concerns of copper corrosion due to a high concentration of ammonia. In addition, in the case where copper is used in a condenser or low pressure feed water heater, all the storage water should be blown after drum storage and yet,  
15 if it has spaces from which water cannot be discharged, either the drum should be sufficiently washed with pure water, or the steam should be released until ammonia concentration drops below a predetermined level after starting boiler operation and then steam supply begins. Furthermore, in a boiler which has a superheater and in which the  
20 recovery ratio of condensate is 50% or more, when the drum is stored with amine, neutralizing amine is mixed with operating water, organic acid or carbon dioxide is produced by thermal decomposition of the amine, the pH of feed water condensate, or boiler water is decreased, the acid conductivity of the feed water or steam is increased and there is  
25 a possibility that the boiler operation will be troubled. However, because there are no such concerns with the present invention, the present invention can be suitably applied.

[0032]

In this way, in the case where a boiler which is filled with an  
30 ammonia water is stored over a long period of time, regular checks are

preferred. For example, the pH, concentration of ammonia or an iron ion as a corrosive substance should be checked about once or twice a month, and in the case where it is recognized that the pH, concentration of ammonia, or concentration of iron ion has increased, adding ammonia into the boiler is preferred. In this case, one part of the storage water is blown and water is supplied while adding ammonia so that the concentration of ammonia within the boiler drum becomes a predetermined concentration. At this time, it is preferable to heat and convect the storage water within the boiler drum when one part of the storage water is extracted from the boiler so that the concentration of ammonia in the storage water within the boiler drum becomes uniform.

[0033]

Apart from ammonia other known boiler water treatment additives may be added according to necessity to the soft water or pure water which fills the boiler.

[0034]

As a boiler water treatment additive, for example, diethyl hydroxylamine, isoprophylamine, 1-aminopyrrolidine, 1-amino-4-methylpiperazine, carbonylhydrazide, trisodium phosphate, disodium hydrogen phosphate, sodium tripolyphosphate and sodium hydroxide can be used alone or two or more can be selected and added.

[0035]

When operation of a boiler is started again after a shut down period, all or one part of the storage water is blown according to necessity, and then it is filled with water and operation is started. At this time, according to necessity, a boiler compound or deoxidizer can also be introduced.

[0036]

The storage water which is blown is allowed to discharge after treating so that it meets a certain water emission standard.

[0037]

Furthermore, it is preferred that hydrazine or sodium nitrite not be used.

## 5 Example 1

[0038]

The present invention will be explained in further detail below with specific examples. However, the present invention is not limited to these examples. In the examples 1 to 7, the chemicals shown in table 10 1 were added to pure water and made 500 ml, and the mixture was put into a 500 ml resin beaker, two steel test pieces (1 mm X 30 mm X 50 mm) were immersed in this mixture, the upper part of the beaker was sealed with a resin sheet and the beaker was left to rest at room temperature. After a period of time shown in table 1 had passed, the 15 test pieces were taken out and visually inspected to check the existence of rust. The results are shown in table 1. In the table, MEA indicates monoethanolamine, MIPA indicates monoisopropanolamine and CHA indicates cyclohexylamine.

[0039]

20 Other than not adding a chemical agent for corrosion prevention tests, comparative example 1 was conducted under the same conditions as the examples. Other than using known amines with neutralizing properties instead of ammonia, comparative examples 2 to 12 were conducted under the same conditions as the examples.

25 [0040]

(TABLE1)

|                       | Ammonia<br>(mg/L) | MEA<br>(mg/L) | MIPA<br>(mg/L) | CHA<br>(mg/L) | Period  | Corrosion<br>rate(mdd) |
|-----------------------|-------------------|---------------|----------------|---------------|---------|------------------------|
| Comparative example 1 | —                 | —             | —              | —             | 1 month | 5.30                   |

|                        |     |      |     |     |           |       |
|------------------------|-----|------|-----|-----|-----------|-------|
| Comparative example 2  | —   | 300  | —   | —   | 12 months | 0.35  |
| Comparative example 3  | —   | 400  | —   | —   | 1 month   | 0.10  |
| Comparative example 4  | —   | 400  | —   | —   | 4 months  | 0.04  |
| Comparative example 5  | —   | 400  | —   | —   | 12 months | 0.01  |
| Comparative example 6  | —   | 500  | —   | —   | 12 months | 0.04  |
| Comparative example 7  | —   | 1000 | —   | —   | 12 months | 0.02  |
| Comparative example 8  | —   | —    | 200 | —   | 4 months  | 1.45  |
| Comparative example 9  | —   | —    | 400 | —   | 4 months  | 0.13  |
| Comparative example 10 | —   | —    | 600 | —   | 4 months  | 0.05  |
| Comparative example 11 | —   | 30   | —   | 100 | 4 months  | 0.07  |
| Comparative example 12 | —   | 90   | —   | 300 | 4 months  | 0.03  |
| Example 1              | 30  | —    | —   | —   | 1 month   | 0.06  |
| Example 2              | 30  | —    | —   | —   | 4 months  | 0.02  |
| Example 3              | 300 | —    | —   | —   | 1 month   | 0.05  |
| Example 4              | 300 | —    | —   | —   | 4 months  | 0.01  |
| Example 5              | 300 | —    | —   | —   | 12 months | <0.01 |
| Example 6              | 500 | —    | —   | —   | 4 months  | <0.01 |
| Example 7              | 500 | —    | —   | —   | 12 months | <0.01 |

[0041]

From the results shown in table 1, in the examples 1 to 7 which used ammonia of the present invention, compared to amines with neutralizing properties of the comparative examples, it was found that the same or greater corrosion prevention effects could be obtained with a less amount of additive.

[0042]

The operation method of a resting boiler which is proposed by the present invention can be applied to an arbitrary boiler such as a cylindrical boiler, a water tube boiler, a through flow boiler and a circulation boiler. In addition, because the chemical agent which is

used is ammonia which is registered as a food additive, it can be applied even in the case where steam comes into direct contact with the human body or food products.

## CLAIMS

1. A method of corrosion prevention for a resting boiler comprising:  
shutting down a boiler which is operated, said boiler being  
5 supplied with dehardnees water; and then,  
filling a drum of said boiler with a storage water which is obtained  
by adding ammonia to dehardness water, and storing.
2. The method of corrosion prevention for a resting boiler according  
10 to claim 1, wherein said dehardness water is a pure water,  
supplying water which is obtained by adding ammonia to a boiler  
water, said boiler water being held in said boiler drum, to the inside of  
said boiler drum as said storage water.
- 15 3. The method of corrosion prevention for a resting boiler according  
to claim 1, wherein  
discharging a boiler water from the inside of said boiler drum;  
and then,  
supplying a water which is obtained by adding ammonia to  
20 dehardness water to the inside of said boiler drum as said storage  
water.
4. The method of corrosion prevention for a resting boiler according  
to any one of claims 1 to claims 3, wherein said boiler is made from  
25 steel.