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(54) CLEANING AGENTS FOR REMOVING SCALES

- (71) We, KURITA WATER INDUSTRIES, LTD., (formerly Kurita Industrial Co., Ltd.) of No. 1, 3-chome, Koraibashi, Higashi-ku, Osaka-shi, Japan, a Japanese body corporate do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—
- 5 The present invention relates to cleaning compositions of cleaning agents which can remove copper-containing scales from metal surfaces, e.g. those of water-heating systems, by a simple method and in a short time.
- 10 When copper or alloys of copper are used together with steel in the system of a boiler, heat-exchanger, and other apparatus, copper and copper oxides are found in considerable quantities in the scales deposited on the surfaces of the vessel or tube in which water is heated. With regard to the removal of such copper components formed in the scales, a cleaning method using an ammonia solution containing oxidant and a cleaning method with the use of the acid solution containing a copper dissolving agent have been widely known and used. When cleaning with the use of an ammonia solution containing an oxidant, however, the copper components in the scales can be eliminated, but iron oxides which commonly form the greater part of the scales cannot be removed. It is therefore further necessary to conduct the cleaning by means of an acid solution in order to remove the remaining scales, which makes the cleaning work intricate and requires more time for cleaning, the use of such a method being a waste of time, labor and money. On the other hand, cleaning with the use of the acid solution, which contains a copper dissolving agent such as thiourea, dissolves and removes iron oxide and also copper and copper oxide in the scales at the same time. The method, however, removes only a very small amount of copper and can be applied only to scales which contain only a small quantity of copper or where the deposit is slight. Such being the case, in the cleaning of the boilers in a steam electric power-plant, where the scales contain much copper, an ammonia solution is generally used. Thiourea or its derivatives are conventionally used as a copper dissolving agent when the cleaning is done with the use of an acid solution, of which compounds dimethyl thiourea or thiourea being most widely used. They have an excellent dissolving effect on copper and show satisfactory results in promoting the dissolution of copper in the acid solution, especially in an hydrochloric acid solution. However, because the solubility of the compounds of copper and dimethyl thiourea or thiourea contained in the solution is not high, they form a milk-white precipitate in the acid cleaning solution. The precipitate deposits on the tube surface of the boiler or heat-exchanger or similar apparatus, thus reducing the cleaning effect to a great extent. This tendency is particularly displayed when the concentration of iron ions or copper ions in the solution is high.
- At the time of cleaning with the acid solution, the reducing agent, inorganic or organic, such as stannous chloride and L-ascorbic acid, are used to prevent the corrosion or decay of steel due to the oxidation effect of the oxidizing ions such as Fe^{3+} occurring in the solution as a result of the use of the acid cleaning agent. However, under the conditions in which these reducing agents exist together, the milk-white precipitate, which is composed of the compound (complex salt) of copper and copper dissolving agents, such as thiourea and thiourea derivatives, is formed in greater quantity than when the reducing agents are not present in the solution. This lessens not only the dissolving effect on the copper contained in the scales but also the dissolving effect on the whole scales.
- Such being the case, there have been no cleaning methods which are satisfactory enough to remove the copper containing scales in a simple and yet highly efficient procedure; and such a method has long been hoped for.
- The object of the present invention is to provide a composition and procedure by which

the copper containing scales will be removed in a simple method and with highly satisfactory results.

The present invention provides a cleaning composition suitable for removing scales contain copper and iron from metal surfaces, said composition comprising at least one compound selected acid comprising an aqueous solution containing at least one acid; at least one compound of the group consisting of thiourea and thiourea derivatives and at least one compound of the group consisting of hydrazine and hydrazine compounds, the concentration of thiourea and/or thiourea derivative being 0.5 to 10% and the hydrazine and/or hydrazine derivative being present to the extent of at least 0.2 mole per mole of thiourea or thiourea derivative.

By the use of the compositions of the present invention the scales can be removed by a simple and convenient procedure, in a shorter time, with highly satisfactory results; and a further contribution of this improved procedure is the prevention of the development of the corrosion on the surface of the metal surface, for example steel, to which the compositions are applied.

The acid forms the basis of the composition of the cleaning agent and an inorganic acid is preferably used for the purpose. Inorganic acids that can be used in preparing the compositions according to the present invention include hydrochloric acid, sulfuric acid, phosphoric acid and sulfamic acid.

Thiourea and thiourea derivatives are copper dissolving agents and are believed to combine with copper to form thiourea copper complexes and thiourea derivative copper complexes, thus promoting the dissolution of copper. Preferred thiourea derivatives which can be used in this invention are alkylthioureas and phenylthioureas, especially dimethyl thiourea, diethyl thiourea, and diphenyl thiourea.

It is also believed that hydrazine and hydrazine compounds act as solubilizers which increases the solubility of the complexes in the acid solution. Commercially obtainable hydrazine compounds that can be used include: hydrazine hydrochloride, hydrazine sulfate, hydrazine phosphate, hydrazine carbonate, hydrazine maleate, and hydrazine citrate. If desired, two or more of the respective copper dissolving agents and solubilizers mentioned in the foregoing can be used together.

The composition can be used together with any of the conventionally well known corrosion inhibitors, if occasion requires. As for corrosion inhibitors, such commercially obtainable corrosion inhibitors for pickling agents as "Ibit" (trade name of the product manufactured by Sumitomo Chemical Co., Ltd.), "Rodine", (registered trade mark manufactured by Nippon Paint Co., Ltd.), hexamethylenetetramine and thiocyanates may be mentioned. In practical use, they are used singly or in a

certain combination of two or more.

As for the acids in the compositions of the cleaning agents according to the present invention, hydrochloric acid is preferably used and its concentration should preferably range between 0.1% and 20%, and most desirably between 3% and 10%. The main purpose of the acids is to dissolve the iron oxide in the scales. (In this specification all concentrations and percentages are by weight).

The concentration of thiourea and/or thiourea derivatives is 0.5—10%. These substances act upon copper in the presence of an acid to form complex salts and dissolve copper in the solution of the cleaning agent. At least 0.2 mol., and preferably 0.25 to 0.5 mol., of hydrazine or hydrazine derivatives are added per mol. of thiourea or thiourea derivatives. These substances act upon the complex salt, which is formed of thiourea or thiourea derivatives and copper, and promote the dissolution of copper by enhancing the solubility of this complex salt in the acid solution, and consequently hydrazine or hydrazine derivatives are believed to prevent the precipitation of this complex salt.

At the same time, hydrazine or hydrazine compounds, which are endowed with reducing power, have a function to prevent the steel from suffering corrosion due to the oxidizing ions, such as Fe^{3+} , which are formed, and further they are believed to have the ability of promoting the reaction forming the complex of copper ions and thiourea or thiourea derivatives.

By the use of the compositions of the present invention, Cu^{2+} and Cu^+ are prevented from corroding the steel and their electro-deposition on the surface of the steel is also prevented. A view may accordingly be held that, in cleaning agents having this composition, thus the respective components co-operate with one another, thus producing an excellent cleaning effect on the scales.

In the compositions of the present invention, the solubility of the compound (complex salt) of the copper dissolving agent and copper is greatly increased when the cleaning composition is made by adding a copper dissolving agent of thiourea or thiourea derivative to the acid solution, and further adding hydrazine as the hydrate or other hydrazine compound to the acid solution thus obtained. Said compositions therefore exhibit outstanding efficacy as a cleaning agent to remove the scales which contain a great deal of copper components such as copper or copper oxide. This is especially so when the compositions are used to remove the scales formed in the boiler of the steam electric-power plant which contain a great deal of the copper scale components such as copper foils found in the iron oxide scales. Even the removal of such scales that have hitherto required ammonia cleaning as an indispensable cleansing process can now be completed in a

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single process of acid cleaning and that in a very short time. Moreover, since hydrazine or hydrazine compounds which are added to the cleaning agent have a reducing power, they prevent steel from being attacked by the corrosion of the oxidizing ions such as Fe^{3+} introduced into the acid solution.

Examples of the compositions and the procedure of the invention will now be given (in Examples 3, 7 and 8) in comparison with known compositions (in Examples 1, 2 and 4 to 6). The cleaning compositions and the results are given in Tables 1 and 2.

EXAMPLES 1 TO 5

The scales dissolving test was conducted with a boiler tube 7cm in length cut from the boiler in a steam electric-power plant. The water-contacting surfaces of the tube were covered with scales of average weight 23 mg/cm² consisting of 50% Fe_2O_3 , 20% CuO , 10.5% ZnO , 4.5% NiO , 1.2% SiO_2 and 1.5% $MgO + CaO$. Both ends of the sample tube were respectively fitted tightly to flanges made of stainless steel and connected with rubber tubes with the aid of a rubber packing between the sample tube and the flange so that the cleaning composition might be stirred and circulated through the sample tube and a glass flask to which the rubber tubes were connected, the mouth of which was stoppered tightly with a rubber stopper to exclude the outside air. A nitrogen gas stream of high purity was used to stir the cleaning composition (which was charged into the flask and sample tube) once an hour so that the solution in the sample tube might mix well with the solution in the glass flask. At the end of the test, having mixed the contents of the tube and flask thoroughly, a stopcock fitted to the flask was opened to take out the sample solution, which was then analyzed to determine the iron and copper ions present. Immediately after the treatment was over, the flanges and packings were taken from the sample tube, and the removal of the scales was examined with the naked eye.

The amount of the chemical solution used in the aforementioned test was 2.5 ml. per 1 cm² of the water contacting surfaces of the sample tube. The desired temperature of the cleaning agent was kept by putting the sample tube fitted with the flanges in a thermostatic water bath. The results obtained from the test conducted with the solution kept at 60°C for six hours are shown in Table 1.

The "corrosion rate" and "removal percentage of scales" in the above table were

measured by the following methods:

Corrosion rate

A specimen of mild steel for the boiler (with the surface area of 25 cm²) was put in the solution together with the boiler tube and weight loss after the test was measured and the corrosion rate was represented by unit time, unit area, and weight loss as in the following formula,

$$\frac{\text{weight loss of the specimen, (mg)}}{\text{Area of the specimen (cm}^2\text{). Testing time, (hr)}}$$

Removal percentage of scales:

The ratio of the area where the scales were removed to the area which had been covered with the scales before the test was observed with the naked eye (%)

$$\frac{\text{Area exposed due to removed scales}}{\text{Area covered by scales before test}} \times 100$$

As seen from the test results mentioned above, the cleaning agent with hydrazine contained in it showed much better performance than that containing other reducing agents. It is believed that hydrazine does not work exclusively as a reducing agent in the solution however, since the procedure is required to remove copper in the acid solution, copper or copper oxides, whether mixed in the iron oxide or existing between the layers of the iron oxide, is easily removed, unlike the ammonia solution method, because the iron oxide is dissolved and removed by the acid.

EXAMPLES 6 TO 8

The same procedure of Examples 1 to 5 was performed with a length of boiler tube from a boiler in the steam electric-power plant which was covered with scales to the extent of 50 mg/cm² in average consisting of 34% Fe_2O_3 , 25% CuO , 36% ZnO , 3.6% NiO . As for hydrazine compounds, hydrazine hydrochloride was used in an amount of 3.5 ml/cm² in the test solution. The results thus obtained in the test are shown in Table 2.

From the figures mentioned in table 2, it is clear that satisfactory results are obtained when at least 1/5 mol. calculated in terms of hydrazine, of hydrazine or hydrazine compounds, is added per mol. of thiourea component.

TABLE 1

Example	Composition of cleaning agent		Amount of ion dissolved ppm		Corrosion rate (mg/cm ² /hr)	Removal percentage of scales
	Chemicals	Concentration	Fe	Cu		
1	Hydrochloric acid	5%				
	Thiourea	1/4 mol/l	3,750	1,100	0.15	85%
	Ibit 1—L	0.5%				
2	Hydrochloric acid	5%				
	Thiourea	1/4 mol/l				
	Hexamethylene- tetramine	0.2%	3,400	850	0.09	80%
	Ibit 1—L	0.5%				
3	Hydrochloric acid	5%				
	Thiourea	1/4 mol/l				
	Hydrazine hydrate	1/20 mol/l	3,300	1,550	0.012	100%
	Hexamethylene- tetramine	0.2%				
	Ibit 1—L	0.5%				

TABLE 1 (Continued)

Example	Composition of cleaning agent		Amount of ion dissolved (ppm)		Corrosion/rate (mg/cm ² /hr)	Removal percentage of scales
	Chemicals	Concentration	Fe	Cu		
4	Hydrochloric acid	5%				
	Thiourea	1/4 mol/l				
	Stannous chloride	1/20 mol/l				
	Hexamethylene- tetramine	0.2%				
5	Ibit 1--L	0.5%	3,300	850	0.012	85%
	Hydrochloric acid	5%				
	Thiourea	1/4 mol/l				
	L-ascorbic acid	1/20 mol/l				
	Hexamethylene- tetramine	0.2%				
	Ibit 1--L	0.5%	3,150	900	0.012	85%

TABLE 2

Example	Composition of cleaning agent		Amount of ion dissolved (ppm)		Corrosion rate (mg/cm ² /hr)	Removal percentage of scales
	Chemicals	Concentration	Fe	Cu		
6	Hydrochloric acid	5%				
	Thiourea	2/5 mol/l				
	Hydrazine hydrochloride	1/15 mol/l	2,700	1,750	0.12	90 — 95%
	Hexamethylene-tetramine Ibit 1—L	0.2% 0.5%				
7	Hydrochloric acid	5%				
	Thiourea	2/5 mol/l				
	Hydrazine hydrochloride	2/25 mol/l	2,300	2,560	0.11	100%
	Hexamethylene-tetramine Ibit 1—L	0.2% 0.5%				
8	Hydrochloric acid	5%				
	Thiourea	2/5 mol/l				
	Hydrazine hydrochloride	1/10 mol/l	2,350	2,600	0.11	100%
	Hexamethylene-tetramine Ibit 1—L	0.2% 0.5%				

WHAT WE CLAIM IS:—

1. A cleaning composition suitable for removing scale containing copper and iron from metal surfaces, said composition comprising:
 - a) at least one acid;
 - b) at least one compound of the group thiourea and thiourea derivatives; and
 - c) at least one compound of the group hydrazine and hydrazine compounds;
- the hydrazine and/or hydrazine compound being present in a concentration of at least 0.2 mole per mole of thiourea or thiourea derivative the concentration of thiourea and/or its derivative being from 0.5 to 10% and
2. A composition as claimed in claim 1, in which the acids are inorganic acids.
3. A composition as claimed in claim 2, in which the acid is at least one of hydrochloric, sulphuric, phosphoric and sulfamic acids.
4. A composition as claimed in any preceding claim, in which the thiourea derivatives are alkyl and phenyl derivatives.
5. A composition as claimed in claim 4, in which the thiourea derivatives are the dimethyl, diethyl and diphenyl derivatives.
6. A composition as claimed in any preceding claim, in which the hydrazine compounds are the hydrate and the hydrochloride, sulphate, phosphate, carbonate, maleate and citrate.
7. A composition as claimed in any preceding claim, in which the acid is hydrochloric acid present in a concentration from 0.1 to 20%.
8. A composition as claimed in claim 7, in which the acid concentration is from 3% to 10%.
9. A composition as claimed in any of claims 1 to 8, in which the concentration of hydrazine and/or its compound is from 0.25 to 0.5 mole per mole of thiourea or its derivative.
10. A composition as claimed in claim 1, substantially as described in any of Examples 3, 7 or 8.
11. A process for the removal of copper containing scales in water heating systems in which the surface carrying the scales is contacted with a composition claimed in any preceding claim.
12. A surface treated by the process claimed in claim 11.

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