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(54) Composition and method for simultaneously removing iron and copper scales from ferrous metal surfaces.

(57) Compositions for simultaeously removing iron and copper scales from ferrous metal surfaces comprise water, one or more organic chelating acids which dissolve iron, one or more reducing agents selected from erythorbic acid, alkali metal salts of erythorbic acid, and ammonium salts of erythorbic acid, and, as copper complexing compound, thiourea and/or hexahydropyrimidine-2-thione. The compositions are utilized by contacting scale-containing ferrous metal surfaces therewith at temperatures of from about 75°F (24°C) to about 150°F (66°C).

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COMPOSITION AND METHOD FOR SIMULTANEOUSLY REMOVING IRON AND COPPER SCALES FROM FERROUS METAL SURFACES

This invention relates to a method of simultaneously removing iron and copper scales from ferrous metal surfaces, and to compositions useful therefor.

In the operation of high pressure steam generating equipment utilized in electric power generation and other applications, the interiors of boiler tubes generally always gradually become encrusted with scale deposits consisting primarily of ferric oxide, e.g. magnetite (Fe_3O_4) and hematite (Fe_2O_3). Copper oxide scale is also usually present and copper metal is often plated directly onto the boiler tube walls.

Removal of iron and copper scales from boiler tubes and other scale-containing ferrous metal surfaces with acidic formulations to dissolve the scales. One such acidic composition which has found wide usage in removing iron scales from industrial boiler and other heating surfaces is an aqueous mixture of hydroxyacetic acid and formic acid. However, the hydroxyacetic-formic acid mixture has heretofore had to be used at high temperatures, i.e. about 200°F (93°C) with constant agitation in order to efficiently remove the scales. Because of the high temperatures involved, copper complexing chemicals have not been included in the composition, and consequently, a separate step has been required for removing copper scales. That is, the aqueous mixture of hydroxyacetic and formic acids has been removed from contact with a scale-containing surface after iron scales thereon have been dissolved, and a second composition containing a copper complexor has then been brought into contact with the scale-containing surface at a lower temperature to remove copper scales. This two-step procedure has been necessitated by the fact that the copper complexors degrade and are ineffective at temperatures above about 160°F (71°C).

We have now found that iron and copper scales can be removed simultaneously from ferrous metal surfaces.

According to the present invention, there is provided a composition for simultaneously removing iron and copper scales from a ferrous metal surface, which comprises water; one or more organic chelating acids which dissolve iron; one or more reducing agents selected from erythorbic acid, and alkali metal salts and ammonium salts of erythorbic acid; and as copper complexor, one or both of thiourea and hexahydropyrimidine-2-thione.

The invention also includes a method of simultaneously removing iron and copper scales from a ferrous metal surface which comprises contacting said scale-containing ferrous metal surface with a composition of the invention, and maintaing said contact for a time and at a temperature sufficient for said scales to be dissolved.

Any organic acid, or mixture of organic acids, having low pH (a pH of less than 7 at room temperature) which chelate iron can be used in the compositions of this invention. Examples of suitable such acids are hydroxyacetic acid, formic acid, malic acid, citric acid, ethylenediaminetetracetic acid (EDTA), nitrilotriacetic acid, and mixtures of such acids. Of the various organic iron chelating acids which can be used, a mixture of hydroxyacetic acid and formic acid is preferred.

The organic iron chelating acid or acids utilized in the aqueous scale-removing compositions of this invention are preferably present in an amount of from 1% to 10% by weight of the compositions. The preferred acids, i.e.

hydroxyacetic acid and formic acid, are preferably present in the aqueous compositions in a weight ratio of hydroxyacetic to formic acid of about 2:1.

The erythorbic acid and/or salt reducing agent functions in the compositions of this invention to increase the rate of dissolution of iron by the organic chelating acid or acids utilized, whereby iron scales can be effectively removed from ferrous surfaces by the compositions at low temperatures, i.e. temperatures in the range of from about 75°F (24°C) to about 150°F (66°C). This, in turn, allows copper complexing compounds to be included in the compositions whereby both iron and copper scales are simultaneously removed by the compositions. As indicated above, the reducing agents utilized in the compositions are selected from the group consisting of erythorbic acid, alkali metal salts of erythorbic acid, ammonium salts of erythorbic acid and mixtures thereof and are preferably included in the compositions in an amount in the range of from about 0.25% to about 5% by weight of the compositions. Most preferably, the reducing agent is sodium erythorbate and is present in the aqueous compositions in an amount of 1% by weight of the compositions.

The copper complexing compounds utilized in the compositions of this invention are thiourea and hexahydropyrimidine-2-thione. A mixture of the two can be used. The copper complexor is preferably included in the aqueous composition in an amount of from 0.25% to 3% by weight of the compositions. Preferably, the copper complexor is a mixture of hexyhydropyrimidine-2-thione and thiourea consisting of 60 parts by weight hexahydropyrimidine-2-thione and 40 parts by weight thiourea, present in the aqueous composition in an amount of about 1% by weight.

A particularly preferred composition of this invention is comprised of water, hydroxyacetic acid present in the composition in an amount of about 2% by weight of the composition, formic acid present in the composition in the amount of about 1% by weight of the composition, sodium erythorbate present in the composition in an amount of about 1% by weight, and a mixture of 60 parts by weight hexahydropyrimidine-2-thione and 40 parts by weight thiourea present in the composition in an amount of about 1% by weight.

Various ferrous metal corrosion inhibitors can be included in the compositions of this invention, as for example, dibutyl-thiourea, quaternary alkyl pyridinium salts, alkylbenzene sulfonate and heavy aromatic naphtha. The most preferred ferrous metal corrosion inhibitor for use in accordance with this invention is a low chloride inhibitor mixture comprised of 15% by weight heavy aromatic naphtha, 40% by weight ethylene glycol, 8% by weight dibutyl thiourea, 12% by weight acetic acid, 10% by weight alkyl pyridine, 10% by weight nonionic ethoxylated alcohol and 5% by weight ethoxylated amine. The corrosion inhibitor is preferably included in the aqueous composition in an amount of from about .05% to about 6% by volume of the composition.

In carrying out the methods of the present invention for simultaneously removing iron and copper scales from ferrous surfaces, a composition of the present invention is brought into contact with an iron and copper scale-containing ferrous metal surface at a temperature and for a time sufficient for the scales to be dissolved by the composition and thereby removed from the surface. The composition containing the dissolved scales is removed from contact with the surface and disposed of in the usual manner whereby pollution of the environment does not result.

As mentioned above, the temperature of the aqueous composition during the contact of the scale-containing surfaces can be as low as 75°F (24°C) while still efficiently removing scale from the surfaces up to as high as about 150°F (66°C). At temperatures above about 150°F (66°C), degradation of the copper complexors begins to take place. The most preferred contact temperature is about 140°F (60°C).

As is well understood by those skilled in the art, the cleaning compositions can be brought into contact with the scale-containing surfaces in a static condition, or as is preferred, the compositions can be circulated over the surfaces. The compositions effectively dissolve deposits containing iron and copper at temperatures in the range of from about 75°F (24°C) to about 150°F (66°C) in a single stage treatment.

In order to facilitate a clearer understanding of the methods and compositions of the present invention, the following Examples are given by way of illustration only.

Example 1

Aqueous solutions containing 2% by weight hydroxyacetic acid, 1% by weight formic acid and 0.1% by volume of a corrosion inhibitor are prepared. One hundred milliliter portions of the solutions are placed in glass beakers, 2 grams of powdered iron oxide (technical grade magnetite) are added thereto and dry pre-weighed 1020 mild steel corrosion coupons are placed in the solutions. Various quantities of sodium erythorbate are added to some of the test solutions, the solutions are heated to the temperatures given in Table 1 below and the solutions are maintained at such temperatures for time periods of six hours. During the six hour periods, the test solutions are stirred for one minute each hour and at the termination of the six hour periods, the solutions are analyzed for dissolved iron (by atomic absorption analysis) and the weight losses of the corrosion coupons are determined. The results of these tests are given in Table I below.

The corrosion inhibitor is a commercially available mixture comprised of 15% by weight heavy aromatic naphtha, 40% by weight ethylene glycol, 8% by weight dibutyl thiourea, 12% by weight acetic acid, 10% by weight alkyl pyridine, 10% by weight nonionic ethoxylated alcohol and 5% by weight ethoxylated amine.

TABLE I

Magnetite Dissolution Tests in Aqueous Hydroxyacetic-Formic Acid Solutions with and without Sodium Erythorbate

Test No.	Sodium[1] Erythorbate %	Temperature, °F	(°C)	Mild Steel Corrosion Rate lbs/ft²/day	g/m²/day	Magnetite[2] Dissolved Grams	Percent
1	0	120	(49)	0.002	9.6	0.015	0.75
2	0	140	(60)	0.003	14.5	0.030	1.5
3	0	160	(71)	0.003	14.5	0.023	1.15
4	0	180	(82)	0.003	14.5	0.037	1.85
5	1	120	(49)	0.001	4.8	0.214	10.7
6	1	140	(60)	0.001	4.8	0.265	13.25
7	1	160	(71)	0.002	9.6	0.344	17.2
8	1	180	(82)	0.003	14.5	0.400	20.0
9	2	120	(49)	0.001	4.8	0.237	11.85
10	2	140	(60)	0.001	4.8	0.355	17.75
11	2	160	(71)	0.002	9.6	0.419	20.95
12	2	180	(82)	0.003	14.5	0.451	22.55

1 The percent number indicated is the number of grams of sodium erythorbate per 100 milliliters of solution.

2 Amount of dissolved magnetite is determined by atomic absorption analysis of spent solvent. This value is corrected for coupon weight loss.

From Table I it is readily apparent that an aqueous solution of hydroxyacetic and formic acids dissolves a greater quantity of magnetite at higher temperatures. However, it is also readily apparent that the inclusion of sodium erythorbate in an aqueous solution of hydroxyacetic and formic acids brings about an increase in the dissolution of magenetite. For example, at 120°F (49°C) the inclusion of 1% by weight sodium erythorbate results in a 14-fold increase in the quantity of magnetite dissolved (tests 1 and 5). A 2% concentration of sodium erythorbate results in a 16-fold increase in the dissolution of magnetite (tests 1 and 9). At 140°F (60°C), a solution without sodium erythorbate dissolves twice as much magnetite as does the same solution at 120°F (49°C)(tests 1 and 2). The same aqueous solution with 1% sodium erythorbate at 140°F (60°C) results in an 18-fold increase in magnetite dissolution as compared to the solution without sodium erythorbate at 120°F (49°C) (tests 1 and 6). Thus, the inclusion of sodium erythorbate in the aqueous hydroxyacetic-formic acid solutions brings about an increase in the rate of dissolution of magnetite which is far greater than the effect of heat alone on the rate of dissolution.

Example 2

One hundred milliliter portions of aqueous solutions containing 2% by weight hydroxyacetic acid, 1% by weight formic acid and 0.1% by volume of the corrosion inhibitor described in Example 1 are placed in glass beakers. Sodium erythorbate and/or copper complexor are combined with some of the solutions and 2 grams of powdered iron oxide (technical grade magnetite) and 0.1 gram of copper powder are combined with the solutions. Dry pre-weighed 1020 mild steel corrosion coupons are placed in the solutions and the solutions are heated and maintained at temperatures of 140°F (60°C) for time periods of six hours with one minute of stirring each hour. At the termination of the six-hour test periods, the solutions are analyzed (by atomic absorption analysis) for dissolved iron and copper and the weight losses of the corrosion coupons are determined.

The results of these tests are given in Table II below.

TABLE II

Copper and Magnetite Dissolution in Aqueous Hydroxyacetic-Formic Acid Solutions with and without Sodium Erythorbate and Copper Complexor at 140°F for 6 Hours

	Additive[3]		Results[2]		
Test No.	Sodium Erythorbate %	Copper[1] Complexor, %	Magnetite Dissolved Grams	Magnetite Dissolved Percent	Copper Dissolved Percent
13	0	0	0.029	1.45	0.0010
14	0	1% "A"	0.045	2.25	0.0240
15	0	1% "A"	0.037	1.85	0.0215
16	1	0	0.270	13.5	0.0015
17	1	1% "A"	0.334	16.7	0.0235
18	1	1% Thiourea	0.456	22.8	0.0223
19	2	1% "A"	0.363	18.15	0.0247
20	2	1% Thiourea	0.373	18.65	0.0222

1 Copper complexor "A" is a mixture consisting of 60% by weight hexahydropyrimidine-2-thione and 40% by weight thiourea.

2 Amounts of dissolved magnetite and copper are determined by atomic absorption analysis of spent solvent. The value of dissolved magnetite is corrected for coupon weight loss.

3 The percent number indicated is the number of grams of additive per 100 milliliters of solution.

From Table II it can be seen that the addition of a copper complexor to an aqueous solution of hydroxyacetic acid, formic acid and sodium erythorbate does not diminish the ability of the solution to dissolve magnetite at 140°F (60°C) (see tests 6 and 10 of Table I and 17, 18, 19 and 20 of Table II) but, in fact, increases the amount of magnetite dissolved. The addition of the copper complexor to an aqueous solution of hydroxyacetic and formic acids in the absence of sodium erythorbate (tests 13, 14 and 15), produces a small increase in the dissolution of magnetite, but the dissolution of copper is greatly increased. When sodium erythorbate and copper complexor are both present in the aqueous solution (tests 17, 18, 19 and 20), greatly improved dissolution of both magnetite and copper are obtained as compared to when neither additive or only one is present, i.e., tests 2, 6, 10, 13, 14, 15, and 16.

Example 3

Small sections of boiler tube containing iron and copper scale are placed in glass beakers, each of which contains 225 milliliters of an aqueous solution containing 2% by weight hydroxyacetic acid, 1% by weight formic acid and 0.1% by volume of the corrosion inhibitor described in Example 1. Some of the solutions also contain sodium erythorbate and copper complexor. The solutions are heated to temperatures of 140°F (60°C) and maintained at such temperatures for time periods of 24 hours. At the terminations of the 24 hour test periods, the solutions are analyzed by atomic absorption analysis for iron and copper content and the boiler tube sections are inspected for the presence of scale.

The test sections of boiler tube are cut from two boiler tube samples designated herein as boiler tube sample A and boiler tube sample B. The scale on boiler tube sample A consists a magnetite, copper metal and hydroxyapatite $[Ca_5(PO_4)_3OH]$. The scale on boiler tube sample B consists of magnetite, copper and nickel.

The results of these test are set forth in Table III below.

TABLE III

Scale Removal by Aqueous Hydroxyacetic-Formic Acid Solutions with and without Sodium Erythorbate and Copper Complexor at 140°F for 24 Hours

Boiler Tube Sample	Test No	Formulation: Sodium Erythorbate %	Formulation: Copper Complexor,[1] %	Results: % Cu	Results: % Fe	Results: Tube Appearance
A	21	0	0	0.00019	0.28	copper plated
A	22	0	1	0.0078	0.45	not clean[2]
A	23	1	1	0.0093	0.39	tube clean[3]
B	24	0	0	0.0010	0.39	copper plated
B	25	0	1	0.0280	0.33	hot side not clean[2]
B	26	1	1	0.0230	0.29	90% clean[4]

1 A mixture consisting of 60% by weight hexahydropyrimidine-2-thione and 40% by weight thiourea.

2 All copper removed but about 40% iron oxide was still on tube section.

3 All scale removed.

4 All copper removed, but about 10% iron oxide was still on tube section.

From Table III it can be seen that the formulation containing sodium erythorbate and copper complexor is effective in removing iron and copper scale.

Example 4

One hundred milliliter portions of an aqueous solution containing 2% by weight hydroxyacetic acid, 1% by weight formic acid and 0.1% by volume of the corrosion inhibitor described in Example 1 are placed in three beakers. Two grams of powdered iron oxide are combined with each solution. One percent by weight sodium erythorbate and 1% by weight copper complexor (60% by weight hexahydropyrimidine-2-thione and 40% by weight thiourea) are combined with the first solution which is maintained at a tmperature of 75°F (24°C) for six hours with one minute of stirring each hour. One percent by weight copper complexor only is added to the second solution which is also maintained at 75°F (24°C) for a six-hour time period. The third solution is heated to 190°F (88°C) and is maintained at such temperature for a six-hour time period. At the terminations of the six-hour time periods, the solutions are analyzed for dissolved iron. The results in these tests are shown in Table IV below.

TABLE IV

Iron Dissolution in Aqueous Hydroxyacetic-Formic Acid
Solutions with and without
Sodium Erythorbate and Copper Complexor

Test No.	Sodium[1] Erythorbate %	Copper[1] Complexor, %	Temperature, °F	°C	Magnetite[2] Dissolved %
27	1	1	75	24	0.026
28	0	1	75	24	0.012
29	0	0	190	88	0.027

1 The percent number indicated is the number of grams of additive per 100 milliliters of solution.

2 Amounts of dissolved magnetite and copper are determined by atomic absorption analysis of spent solvent. The value of dissolved magnetite is corrected for coupon weight loss.

From Table IV it can be seen that the solution containing sodium erythorbate and copper complexor effectively dissolves magnetite at 75°F (24°C).

CLAIMS:

1. A composition for simultaneously removing iron and copper scales from a ferrous metal surface, which comprises water; one or more organic chelating acids which dissolve iron; one or more reducing agents selected from erythorbic acid, and alkali metal salts and ammonium salts of erythorbic acid; and, as copper complexor, one or both of thiourea and hexahydropyrimidine-2-thione.

2. A composition according to claim 1, which further includes a ferrous metal corrosion inhibitor.

3. A composition according to claim 2 wherein said ferrous metal corrosion inhibitor is a mixture of heavy aromatic naptha, ethylene glycol, dibutylthiourea, acetic acid, alkyl pyridine, nonionioc ethoxylated alcohol and ethoxylated amine.

4. A composition according to claim 1, 2 or 3, wherein said organic acid or acids are selected from hydroxyacetic acid, acetic acid, formic acid, malic acid, citric acid, EDTA, and nitrilotriacetic acid.

5. A composition according to claim 4, wherein said organic acids are hydroxyacetic acid and formic acid.

6. A composition according to any of claims 1 to 5, wherein said reducing agent is sodium erythorbate, and said copper complexor is a mixture of thiourea and hexyhydropyrimidine-2-thione.

7. A composition according to claim 6, wherein said copper complexor mixture consists of 60 parts by weight hexahydropyrimidine-2-thione and 40 parts by weight thiourea.

8. A composition according to any of claims 1 to 7, wherein said organic acid or acids are present in an amount of from 1% to 10% by weight of the composition, said reducing agent is present in an amount of from 0.25% to 5% by weight of said composition, and said copper complexor is present in said composition in an amount of from 0.25% to 3% by weight of said composition.

9. A method of simultaeously removing iron and copper scales from a ferrous metal surface which comprises contacting said scale-containing ferrous metal surface with a composition as claimed in any preceding claim, and maintaining said contact for a time and at a temperature sufficient for said scales to be dissolved.

10. A method according to claim 9, wherein said scale-containing ferrous metal surface is contacted with said composition at a temperature of from 75°F (24°C) to 150°F (66°C).