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3,490,741

METHOD OF CLEANING METAL SURFACES WITH POLYCARBOXYLIC ACID COMPLEXING AGENTS INHIBITED BY ETHYLENEIMINES OR POLYETHYLENEPOLYAMINES CONTAINING DIVALENT SULFUR

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13 Claims

ABSTRACT OF THE DISCLOSURE

An inhibited aqueous alkaline metal cleaning solution contains from about 0.5 to about 40% of aminopolycarboxylic acid or hydroxypolycarboxylic acid and from 0.005 to about 1% of an inhibitor selected from the group consisting of polyalkyleneamine sulfide, disulfide, and mercaptan; polyalkylenepolyamine sulfide, disulfide, and mercaptan; hydroxyalkylpolyalkyleneamine sulfide; and mixtures thereof with sufficient nitrogen base to bring the solution pH to about 7 to 10 and the balance substantially water. The composition also contains, advantageously, from 0.01 to 0.2% of a complex reaction product of an ammonia derivative, a ketone, an aldehyde and a fatty acid. A metal surface is cleaned substantially without aggravated attack upon the substrate upon bringing the inhibited cleaning solution into contact with the metal.

The invention relates to a novel composition and an improved method of removing iron oxides and hardness deposits from metal surfaces, e.g. those found in high pressure steam boilers, and more particularly is concerned with novel inhibited solutions of polycarboxylic acid chelating or complexing agents suitable for use in said process.

For the purposes of the specification and the appended claims, nitrogen-containing polycarboxylic acid chelating agents as well as polycarboxylic acid metal complexing agents without nitrogen in the molecule are hereinafter referred to as polycarboxylic acid metal complexing agents.

In the removal from metal surfaces of deposits of iron oxide and hardness scale, including carbonates and sulfates of calcium and magnesium, with or without the presence of deposits of copper or copper compounds, cleaning processes have been developed which employ an alkaline solution of a polycarboxylic acid in place of an aqueous mineral acid solution. These polycarboxylic acid chelating or complexing agents, however, have a tendency to corrode the metal substrates while the deposits are being dissolved, especially at regular operating temperatures. It is highly desirable to keep such metal attack to a minimum, the more so where an enclosed vessel or system will be cleaned numerous times during its expected service life.

A principal object of the invention is to provide a method of inhibiting an aqueous alkaline solution of a polycarboxylic acid metal complexing agent whereby corrosive attack of the aqueous solution upon a metal substrate to be cleaned is minimized or even substantially eliminated without interfering with the removal of iron oxides and hardness deposits from the metal, and especially without interfering with the removal of copper deposits.

Another object of the invention is to provide an inhibited metal-cleaning solution suitable for use in the method of the invention.

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These and other objects and advantages of the present invention will be more clearly understood upon becoming familiar with the following description and the illustrative examples.

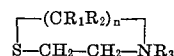
The invention is based on the discovery that an aqueous metal-cleaning solution having a pH in the range of 7 to about 10 and containing from about 0.5 to about 40 percent by weight of a polycarboxylic acid metal complexing agent is inhibited against corrosive attack upon a metal substrate in contact therewith substantially without interfering with the cleaning action of the solution, upon adding to the solution from about 0.005 to 1 percent by weight, preferably from about 0.01 to about 0.5 weight percent and most preferably from about 0.02 to about 0.2 percent by weight of an inhibitor selected from the group consisting of:

(1) $A-S_x-[CH_2CH(R)NH]_n-R_1$ wherein x is 1 or 2, R is hydrogen or lower alkyl, n is an integer in the range of 1 to 8 inclusive, R_1 is hydrogen or lower alkyl, and A is hydrogen, lower alkyl, or $R_2-NH-(CH_2)_m-$ wherein R_2 is hydrogen or lower alkyl and m is an integer in the range of 1 to 8, inclusive;

(2) Hydrosulfide salt of said

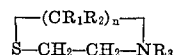


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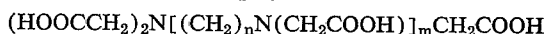
wherein R_1 , R_2 and R_3 are each hydrogen or lower alkyl and n is 1, 2 or 3;

(4) Hydrosulfide salt of said



and

(5) A plurality of such inhibitors in combination. Suitable polycarboxylic acid chelating agents include the alkylene polyamine polyacetic acids of the formula



wherein n may be 1, 2, 3 or 4, and m may be 0, 1, 2, 3 or 4, up to two of the carboxymethyl groups may be replaced with a β -hydroxyethyl group and one or more of the carboxymethyl groups may be replaced by carboxyethyl groups. Specific examples of such acids which are particularly suitable are ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl ethylenediaminetriacetic acid, nitrilotriacetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid, and mixtures thereof. Examples of suitable polycarboxylic acid complexing agents without nitrogen in the molecule are citric acid and tartaric acid.

The inhibitors used in the present invention are substantially all ethyleneimines or polyethylene-polyamines containing divalent sulfur in the molecule. They are normally prepared by the reaction of hydrogen sulfide and ethyleneimine in various proportions, e.g. as described in copending application Ser. No. 463,919, filed June 14, 1965, now Patent No. 3,362,996.

Essentially, each of the inhibitor compounds contains the $S-C-N$ grouping within the molecule. Such compounds are all liquids at substantially ambient room temperature and they are readily soluble in water at the concentrations at which they are employed as inhibitors. Usually these inhibitors are effective and stable up to a temperature of about 200° C. At temperatures below about 60° C. the inhibitors are effective but are usually not needed. The present inhibitors are of advantage be-

cause they do not precipitate from the aqueous cleaning solution of the invention on long standing and they are effective for cleaning times of at least 12 hours.

Examples of specific suitable sulfur-containing amines include bis(2-aminoethyl)sulfide; bis(2-aminoethyl)disulfide; 3-aza-6-thiaoctane-1,8-diamine; beta - mercaptoethylamine; thiazolidine; 2-(aminoethylthio)ethanol; thiazole-2,2-dimethyl thiazole; and the hydrosulfide salts thereof. Suitable classes of sulfur-containing amines are: polyalkyleneamine sulfide, polyalkyleneamine disulfide, polyalkyleneamine mercaptan, hydroxyalkylpolyalkyleneamine sulfide, polyalkylenepolyamine sulfide, polyalkylenepolyamine disulfide and polyalkylenepolyamine mercaptan. Compounds of each of these classes may be used as the hydrosulfide salt.

In an additional embodiment of the present invention there is employed as inhibitor a mixture of one of the compounds described hereinabove with the complex reaction product obtained on bringing together (1) one mole of an ammonia derivative having at least one active hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen, (2) from 1.5 to 10 moles of a ketone having at least one hydrogen atom on the carbon atom adjacent to the carbonyl group, (3) from 2 to 10 moles of an aldehyde selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and (4) from 0.6 to 24 parts by weight based on (1), (2), and (3) of a fatty acid, having from 1 to 20 carbon atoms, at a temperature of from about 150° F. to about 250° F. for from about 1 to 16 hours. Such reaction product is more fully described in U.S. Patent 3,077,454. Generally from about 0.01 to about .2 percent by weight, and more preferably from about 0.03 to about 0.15 percent by weight of such complex reaction product is employed in addition to the amounts of S—C—C—N type inhibitor set forth above.

Use of the combination of the S—C—C—N type inhibitor with the complex reaction product has the advantage of minimizing the amount of total inhibitor needed, since the combination is synergistic in its protection of the metal substrate from corrosion, i.e., the combination is more effective than would have been predicted on a weight basis on considering the likely effect of each inhibitor material acting alone.

The combination has the disadvantage of tending to leave a black colored surface film or finish on the cleaned surface and is not used if a bright surface must be obtained on cleaning.

In yet an additional preferred embodiment of the invention, the present sulfur-containing amine inhibitor having the S—C—C—N grouping is used in combination with the adduct obtained by the chemical combination of equimolar quantities of tall oil fatty acid, epichlorohydrin, and an intralinear ethyleneamine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, and hexaethylenheptamine and mixtures consisting of two or more of such amines in combination. The adduct is prepared by reacting a quantity of tall oil fatty acid with about 10 moles of epichlorohydrin per mole of the fatty acid. The excess of epichlorohydrin after reaction is stripped by a flash distillation. Then a large excess of the intralinear ethyleneamine is added to react with the epoxy product and again the excess is stripped by a flash distillation to leave the desired adduct.

The adduct of the intralinear ethyleneamine is used at a concentration in the range of 0.005 to 0.02 percent by weight, and more preferably at a concentration in the range of 0.001 to 0.01 percent by weight. The sulfur-containing amine used in combination with the adduct of the intralinear ethyleneamine is employed at a concentration in the range of 0.005 to about 1 percent by

weight, but more preferably at the level of about 0.01 to about 0.05 percent by weight. Preferred combinations are (1) bis(2-aminoethyl)sulfide with the adduct of tall oil fatty acid and epichlorohydrin with triethylenetetramine, and (2) bis(2-aminoethyl)sulfide with the adduct of tall oil fatty acid, and epichlorohydrin with tetraethylenepentamine.

For actual use of solutions of these chelating agents in metal cleaning operations, the solutions normally are made alkaline to a pH in the range of 7 to about 10 by addition of the requisite amount of a nitrogen base such as ammonia, an alkanolimine or other suitable amine. Examples of suitable paired combinations of alkylene-polyamine polyacetic acids with nitrogen bases are listed in the following table. (It is to be understood these paired combinations are listed by way of illustration only and are not presented for the purpose of limiting the invention).

Polyacetic acid:	Nitrogen base
EDTA	Ammonia.
EDTA	Ethanolamine.
EDTA	Ethylamine.
EDTA	Ethylenediamine.
EDTA	Diethylenetriamine.
EDTA	Pentaethylenhexamine.
EDTA	Dimethylamine.
EDTA	Trimethylamine.
EDTA	Ethyleneimine.
Ethylenediaminetetrapropionic acid.	Ethanolamine.
N,N - di(β - hydroxyethyl) glycine	Ethylenediamine.
Tetramethylenediamine - N, N,N',N'-tetraacetic acid.	Ammonia.
(α - Hydroxyethylimino) diacetic acid.	Do.

The complexing agents not containing nitrogen in the molecule are similarly combined with a nitrogen base such as ammonia or an amine. Aqueous solutions of these metal complexing agents must normally be employed at a temperature above 90° C. and preferably at a temperature above about 100° C. in order to remove iron oxide and hardness deposits within reasonable times.

In preparing the present inhibited solutions the inhibitor of the invention is readily added at any stage of dissolving or using the polycarboxylic acid metal complexing agent. The inhibitor may be dissolved directly in the water employed before or after adding the polycarboxylic acid, and, ammonia or ammonia derivative. Usually it is convenient to dissolve the inhibitor in sufficient water to make a 1 to 10 percent by weight solution and add the requisite amount of such a pre-mix to the cleaning solution to obtain the concentrations described hereinabove.

In carrying out metal cleaning with the present inhibited cleaning solution the system to be cleaned is filled or otherwise brought into intimate contact with the cleaning solution. The cleaning solution is heated to and ordinarily maintained at a temperature in the range of about 90 to 200° C. until iron oxides and/or hardness deposits are substantially dissolved. At these temperatures, copper deposits or dissolved copper, if present, plate out on the cleaned surface as metallic copper. Copper is dissolved and its complete removal assured by adding an oxidizing agent to the cleaning solution. An oxidizing agent such as sodium nitrite or potassium chromate, or preferably air, is added to the cleaning solution to oxidize the copper to a soluble salt. This is preferably done after the removal of iron oxide and hardness deposits is completed when the temperature of the cleaning solution is reduced to below about 85° C., and preferably to a temperature in the range of about 60 to 70° C.

The cleaning operation is completed by water rinsing the metal surface being cleaned.

A prime advantage of the present invention lies in the effectiveness of the inhibited solution in the dissolution and removal of iron oxides and hardness deposits as well as metallic copper or copper oxide deposits without substantial corrosion of a ferrous metal substrate. The inhibited solution also removes iron oxides and hardness deposits substantially without corroding a copper substrate.

The following examples are presented to illustrate the method and composition of the invention and not to limit the scope thereof.

First series of tests

A series of tests was carried out to illustrate the composition and method of the invention. In each test clean, weighed metal coupons formed of 1010 type carbon steel (SAE) were placed in a glass beaker containing 200 milliliters of an inhibited aqueous solution of EDTA. The solution of EDTA in each case contained 3.8 percent by weight of EDTA, sufficient ammonia to bring the pH of the solution to about 9.2, and one of the inhibitors or inhibitor combinations of the invention. In each test there was employed a pressure reactor consisting of a short section of large diameter pipe having a concave hemispherical-shaped closed end or bottom and a threadable cap closure for the open end. In each case the beaker and solution and coupons were placed in such a pressure reactor and contents were heated to and maintained under autogenous pressure at 95° C. for 4 hours. After the test period, the coupons were removed from the reactor, cleaned, dried and reweighed. Weight losses were extrapolated into pounds per square foot per day (lbs./ft.²/day). The inhibitors employed, the inhibitor concentrations and the weight losses observed are summarized in Table I.

In a control test run by way of comparison, no inhibitor was employed. The results of this test are also listed in Table I.

TABLE I

Test No.	Inhibitor	Weight Percent	Additive, ^a Weight Percent	Corrosion Rate, lbs./ft. ² /day
Control	None			0.0257
1	Mixture A ^b	0.2		0.0014
2	bis(2-aminoethyl)disulfide	0.2		0.0014
3	beta-Mercaptoethylamine	0.2		0.0049
4	bis(2-aminoethyl)sulfide	0.0667	0.133	0.0053
5	bis(2-aminoethyl)sulfide	0.0667	0.133	0.0070
6	beta-Mercaptoethylamine	0.0667	0.133	0.0026
7	do	0.04	0.08	0.0035

^a Additive is the product of reaction of Rosin Amine D, tall oil fatty acids, acetophenone, and paraformaldehyde at a temperature of about 95° C. for about 8 hours in ethylene glycol medium and in the presence of H₂SO₄. After the reaction, an adduct of nonylphenol and ethylene oxide was added to the reaction product. Further see U.S. 3,077,454.

^b Mixture A=70% by weight bis(2-aminoethyl)sulfide plus 30% by weight 3-thia,6-azaoctane,1,8-diamine.

Second series of tests

A second series of tests was carried out in the same manner as the first series, using the inhibited solutions of the invention, except that test temperatures of either 150° or 160° C. were used. Control tests were run by way of comparison, using (1) no inhibitor and (2) the reaction product claimed in U.S. 3,077,454. In a number of tests, replicate runs were made and the results averaged. The inhibitors used, the concentrations thereof, the additive concentrations used and the corrosion rates observed at 150° C. are summarized in Table II. Rates observed at 160° C. are summarized in Table III.

TABLE II

Test No.	Inhibitor	Weight Percent	Additive, ^a Weight Percent	Corrosion Rate, lbs./ft. ² /day
Control	(b)		0.1	0.0302
8	bis(2-aminoethyl)sulfide	0.05	.1	.0006
9	3-thia,6-azaoctane,1,8-diamine	.0335	.067	.0101

TABLE II—Continued

Test No.	Inhibitor	Weight Percent	Additive, ^a Weight Percent	Corrosion Rate, lbs./ft. ² /day
5	10.....do.....	.0367	.0733	.0082
	11.....do.....	.04	.08	.0034
	12.....do.....	.05	.1	.0005
	13.....Mixture B.....	.0335	.067	.0010
	14.....do.....	.0367	.0733	.0007
	15.....do.....	.04	.08	.0006
	16.....H ₂ S salt of bis(2-aminoethyl)sulfide.....	.0335	.067	.0006
10	17.....do.....	.0367	.0733	.0006
	18.....do.....	.04	.08	.0013
	19.....do.....	.05	.1	.0009
	20.....Mixture C.....	.05	.1	.0004
	21.....Mixture D.....	.05	.1	.0011
	22.....Mixture E.....	.05	.1	.0005
	23.....2-(aminoethylthio)ethanol.....	.067	.0335	.0548
15	24.....do.....	.0733	.0367	.0278
	25.....do.....	.08	.04	.0034
	26.....do.....	.1	.05	.0342

^a Additive is the product of reaction of Rosin Amine D, tall oil fatty acids, acetophenone, and paraformaldehyde at a temperature of about 95° C. for about 8 hours in ethylene glycol medium in the presence of H₂SO₄. After the reaction, an adduct of nonylphenol and ethylene oxide was added to the reaction product. Further see U.S. 3,077,454.

^b The "additive" material alone was used and not a sulfur-containing amine according to the invention.

Mixture B=by weight, 90.9 percent of H₂S salt of bis(2-aminoethyl)sulfide and 9.1 percent of ethanol.

Mixture C=by weight, 84.8 percent of bis(2-aminoethyl)sulfide, 1.5 percent of the H₂S salt of bis(2-aminoethyl)sulfide, and 13.6 percent of 3-thia,6-azaoctane,1,8-diamine.

Mixture D=by weight, 84.8 percent of bis(2-aminoethyl)sulfide and 15.1 percent of 3-thia,6-azaoctane,1,8-diamine.

Mixture E=by weight, 84.8 percent of bis(2-aminoethyl)sulfide, 5.2 percent of the H₂S salt of bis(2-aminoethyl)sulfide, and 10.0 percent of 3-thia,6-azaoctane,1,8-diamine.

30	Test No.	Inhibitor	Weight Percent	Additive, ^a Weight Percent	Corrosion Rate, lbs./ft. ² /day
35	Control				0.2730
	Control	(b)		0.1	.0316
	27	bis(2-aminoethyl) sulfide	0.05	.1	.0019
	28	do	.04	.08	.0018
	29	Thiazolidine	.05	.1	.0701
	30	bis(2-aminoethyl)sulfide	.04	.08	.0143
	31	do	.05	.1	.0038
40	32	3-thia,6-azaoctane,1,8-diamine	.05	.1	.0015
	33	Mixture B	.066	.134	.0019
	34	do	.05	.1	.0014
	35	do	.04	.08	.0010
	36	do	.0366	.0733	.0006
	37	H ₂ S salt of bis(2-aminoethyl) sulfide.	.0366	.0733	.0020
	45	38	do	.05	.1
39		Mixture C	.04	.08	.0031
40		Mixture C	.05	.1	.0008
41		Mixture D	.04	.08	.0393
42		do	.05	.1	.0017
43		Mixture E	.04	.08	.0025
44		do	.05	.1	.0009
	45	bis(2-aminoethyl)sulfide	.08	.04	.0147
	46	do	.1	.05	.0507

^a Additive is the product of reaction of Rosin Amine D, tall oil fatty acids, acetophenone, and paraformaldehyde at a temperature of about 95° C. for about 8 hours in ethylene glycol medium in the presence of H₂SO₄. After the reaction, an adduct of nonylphenol and ethylene oxide was added to the reaction product. Further see U.S. 3,077,454.

^b The "additive" material was used and not a sulfur-containing amine according to the invention.

Mixture B=by weight, 90.9 percent of H₂S salt of bis(2-aminoethyl)sulfide and 9.1 percent of ethanol.

Mixture C=by weight, 84.8 percent of bis(2-aminoethyl)sulfide, 1.5 percent of the H₂S salt of bis(2-aminoethyl)sulfide, and 13.6 percent of 3-thia,6-azaoctane,1,8-diamine.

Mixture D=by weight, 84.8 percent of bis(2-aminoethyl)sulfide and 15.1 percent of 3-thia,6-azaoctane,1,8-diamine.

Mixture E=by weight, 84.8 percent of bis(2-aminoethyl)sulfide, 5.2 percent of the H₂S salt of bis(2-aminoethyl)sulfide, and 10.0 percent of 3-thia,6-azaoctane,1,8-diamine.

Third series of tests

A third series of tests was carried out in the same manner as the first and second series, using the inhibited solutions of the invention, except that cleaned and weighed copper coupons were subjected to the solutions instead of steel coupons. Temperatures of 150° and 155° C. were employed. The inhibitors used and the corrosion rates observed are summarized in Table IV. Some of the data represent averaged values for replicate tests.

Control tests were run by way of comparisons using (1) no inhibitor and (2) the reaction product claimed in U.S. 3,077,454. The results of the control tests are also summarized in Table IV.

These tests show that copper surfaces, e.g., heat exchanger tubes in a high pressure steam boiler, are not rapidly attacked by the inhibited cleaning solution of the invention and that the present cleaning process is safely carried out in the cleaning of such boilers.

TABLE IV.—PROTECTION OF COPPER

Test No.	Inhibitor	Weight Percent	Additive, ^a Weight Percent	Temperature, ° C.	Corrosion Rate, lbs./ft. ² /day
Control.....				150	0.0208
Control.....	(b)		0.1	150	.0204
47.....	bis(2-aminoethyl)sulfide (crude).....	.05	.1	150	.0034
48.....	bis(2-aminoethyl)sulfide.....	.05	.1	150	.0008
49.....	Mixture C.....	.05	.1	150	.0018
50.....	Mixture D.....	.05	.1	150	.0008
Control.....				155	.0221
51.....	bis(2-aminoethyl)sulfide.....	.05	.1	155	.0007
52.....	Mixture C.....	.05	.1	155	.0006
53.....	Mixture E.....	.05	.1	155	.0005

^a Additive is the product of reaction of Rosin Amine D, tall oil fatty acids, acetophenone, and paraformaldehyde at a temperature of about 95°C. for about 8 hours in ethylene glycol medium and in the presence of H₂SO₄. After the reaction, an adduct of nonylphenol and ethylene oxide was added to the reaction product. Further see U.S. 3,077,454.

^b The "additive" material was used and not a sulfur-containing amine according to the invention.

Mixture C=by weight, 84.8 percent of bis(2-aminoethyl)sulfide and 1.5 percent of the H₂S salt of bis(2-aminoethyl)sulfide, and 13.6 percent of 3-thia,6-azacotane,1,8-diamine.

Mixture D=by weight, 84.8 percent of bis(2-aminoethyl)sulfide and 15.1 percent of 3-thia,6-azacotane,1,8-diamine.

Mixture E=by weight, 84.8 percent of bis(2-aminoethyl)sulfide, 5.2 percent of H₂S salt of bis(2-aminoethyl)sulfide and 10.0 percent of 3-thia,6-azacotane,1,8-diamine.

Fourth series of tests

In a fourth series of tests, carried out in the same manner as the first and second series, except that the steel coupons were polished, bis(2-aminoethyl)-sulfide was used as the sole inhibitor material, temperatures in the range of about 115 to 171° C. were employed, the test solution contained 10 percent by weight of EDTA and test periods of 16 hours were used. The results of the tests are summarized in Table V.

TABLE V

Test No.	Bis(2-aminoethyl)sulfide Weight, Percent	Temperature, ° C.	Corrosion Rate, lbs/ft. ² /day
54.....	0.01	115	0.0068
55.....	.02	115	.00009
56.....	.05	115	.0051
57.....	.02	128	.0053
58.....	.05	138	.0266

Fifth series of tests

A fifth series of tests was carried out in the same manner as the fourth series except that an intra-linear ethyleneamine adduct was added to all but one of the test solutions. Each of the test solutions contained one of the sulfur-containing amines used in the composition of the invention. The adducts used and the concentration thereof, the concentration of bis(2-amino-ethyl)sulfide used, the temperatures employed and the corrosion rates, extrapolated to a 24 hour basis, are summarized in Table VI. Some adduct and inhibitor combinations were not tested at each of the temperatures.

TABLE VI

Test No.	Adduct Used	Weight Percent	Weight Percent bis(2-aminoethyl)sulfide	Corrosion Rate, lbs./ft. ² /day at—		
				169° C.	137° C.	^a 130° C.
59.....	Adduct A.....	0.005	0.02	0.0036	0.0045	
60.....	do.....	.002	.02	.0097	.0032	^b 0.0029
61.....	do.....	.002	.05		.0045	
62.....	do.....	.02	.02			.0075
63.....	Adduct B.....	.005	.02	.0100	.0052	
64.....	do.....	.002	.02	.0097	.0042	
65.....	do.....	.02	.02			.0080
66.....			.05	.0443	.0214	

^a Tests at this temperature were of 4 hours duration.

^b Average of duplicate runs.

Adduct A=adduct of tall oil fatty acids with epichlorohydrin and triethylenetetramine.

Adduct B=adduct of tall oil fatty acids with epichlorohydrin and tetraethylenepentamine.

Sixth series of tests

A sixth series of tests was carried out in the same manner as the fifth series, except that two mill-scaled coupons and 0.1 gram of CuO were placed in each test

solution along with clean weighed metal corrosion coupons and the contents of the pressure vessel were cooled to 60° C. and air-blown after the 16 hour heating period. In each test bis(2-aminoethyl)sulfide was used at a concentration of 0.02 percent by weight. No scum was found

on any of the coupons at the conclusion of the test when each coupon was rinsed, dried and weighed. The adducts employed, the test temperatures and the corrosion rates observed are listed in Table VII.

TABLE VII

Test No.	Adduct Used	Weight Percent	Temp. of Cleaning, ° C.	Corrosion Rate, lbs./ft. ² /day
67.....	Adduct A.....	0.02	130	^a 0.0038
68.....	do.....	.002	132	.0033
69.....	do.....	.002	130	^a 0.0035
70.....	do.....	.002	120	^a 0.0056
71.....	Adduct B.....	.02	120	

^a Average of duplicate runs.

Adduct A=adduct of tall oil fatty acids with epichlorohydrin and triethylenetetramine.

Adduct B=adduct of tall oil fatty acids with epichlorohydrin and tetraethylenepentamine.

Seventh series of tests

A seventh series of tests was carried out to show the protection of steel coupons during air-blowing. In each case, an inhibited cleaning solution containing 0.02 percent by weight bis(2-aminoethyl)sulfide and one of the intralinear ethyleneamine adducts was used to clean one mill-scaled coupon at 151° C. whereby the chelating agent became partly spent in chelating dissolved iron. In each case, two corrosion coupons and one copper plated coupon were added to the test solution and the test solution was air-blown for 30 minutes at the rate of about

0.004 cubic feet of air per minute. In each case, the coupons were recovered, cleaned, reweighed and inspected. In each case, the extent of corrosion was less than 3.5 milligrams per coupon, and most coupons lost less than 1 milligram. The adducts used, the degree of spentness

of the chelating agent, and the test temperatures are listed in Table VIII.

TABLE VIII

Test No.	Adduct Used	Weight Percent	Percent of Spentness	Test Temp., ° C.
72-----	Adduct A-----	0.005	72	60-66
73-----	do-----	.002	61	60-66
74-----	do-----	.002	74	93
75-----	Adduct B-----	.005	71	60-66
76-----	do-----	.002	70	60-66

Adduct A=adduct of tall oil fatty acids with epichlorohydrin and triethylenetetramine.

Adduct B=adduct of tall oil fatty acids with epichlorohydrin and tetraethylenepentamine.

Eighth series of tests

In yet an additional series of tests, various polycarboxylic acid metal complexing agents are employed, respectively, in cleaning three substantially identical high pressure steam boilers to remove hardness and iron oxide deposits commingled with copper deposits. Each boiler is filled with sufficient cleaning solution to circulate well and reach all critical surfaces, or about 8,000 gallons of solution. Each solution contains about 10 percent by weight of polycarboxylic acid metal complexing agent and 0.02 percent by weight of bis(2-aminoethyl)sulfide. The solution used in the first boiler also contains 0.002 percent by weight of the adduct of tall oil fatty acids, epichlorohydrin and triethylenetetramine. The solution in the first boiler contains EDTA as the polycarboxylic acid complexing agent and the solution has an initial pH of 9 obtained by the addition of the requisite amount of ammonia to the solution. The solution in the second boiler contains nitrilotriacetic acid and the pH has been similarly adjusted. The solution in the third boiler contains citric acid and the initial pH is 7.

The cleaning solution in each boiler is brought to a temperature of 150° C. and maintained at about that temperature for 16 hours while being circulated through the boiler system. During this period substantially all hardness and iron oxide deposits dissolve and copper present in the deposits plates out on the ferrous metal substrate.

Each boiler and its contents is then allowed to cool to about 65° C. The pH of the solution in the third boiler is raised to 9 by the addition of ammonia to the solution. Compressed air is then injected into the solution in each boiler through a port connected to a sparger in the lower part thereof, and vented out the top of the boiler. Such air-blowing continues for about 35 minutes while the temperature is maintained at about 65° C. The solution in each boiler is drained off and each boiler is water rinsed several times with about 10,000 gallons of water per rinse. Each boiler is then opened and inspected. The ferrous metal surfaces are found to be clean and bright and substantially free of pitting and other evidence of corrosive attack by the cleaning solution.

In a manner similar to that set forth for the foregoing examples, inhibited cleaning solution can be prepared using any of the polycarboxylic acids and inhibitors disclosed herein in various combinations within the concentration ranges set forth and these used in accordance with the present novel process.

We claim:

1. A cleaning solution for removing iron oxide and hardness deposits from a metal surface which consists essentially of from about 0.5 to about 40 percent of chelating agent selected from the group consisting of aminopolycarboxylic acid and hydroxypolycarboxylic acid, from about 0.005 to about 1 percent by weight of an inhibitor selected from the group consisting of:

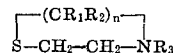
(1) $A-S_x-[CH_2CH(R)NH]_n-R_1$, wherein A is hydrogen, lower alkyl, or $R_2-NH-(CH_2)_m-$ wherein R_2 is lower alkyl and m is an integer in the range of 1 to 8, inclusive, x is one or two, R is hydrogen

or lower alkyl, n is an integer in the range of 1 to 8, inclusive, and R_1 is hydrogen or lower alkyl;

(2) hydrosulfide salt of said



(3)



wherein R_1 , R_2 and R_3 are each hydrogen or lower alkyl and n is 1, 2 or 3;

sufficient nitrogen base selected from the group consisting of ammonia and amine to bring the solution pH to a value in the range of about 7 to 10; and the balance substantially water.

2. The composition as in claim 1 in which the inhibitor is a compound selected from the group consisting of polyalkyleneamine sulfide, polyalkyleneamine disulfide, polyalkyleneamine mercaptan, hydroxyalkylpolyalkyleneamine sulfide, polyalkylenepolyamine sulfide, polyalkylenepolyamine disulfide, polyalkylenepolyamine mercaptan, and mixtures thereof.

3. The composition as in claim 1 in which the inhibitor is bis(2-aminoethyl)sulfide.

4. The composition as in claim 1 in which the concentration of the inhibitor is in the range of 0.01 to 0.5 percent by weight.

5. The composition in claim 1 in which the concentration of the inhibitor is in the range of about 0.02 to about 0.2 percent by weight.

6. The composition as in claim 1 which contains, in addition, from about 0.01 to about 0.2 percent by weight of the product of the reaction of (1) one mole of an ammonia derivative having at least one hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen, (2) from 1.5 to 10 moles of a ketone having at least one hydrogen atom on the carbon atom adjacent to the carbonyl group, (3) from 2 to 10 moles of an aldehyde selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and (4) from 0.6 to 24 parts by weight based on (1), (2), and (3) of a fatty acid having from 1 to 20 carbon atoms at a temperature of from about 150° F. to about 250° F. for from 1 to 16 hours.

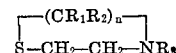
7. The improved method of cleaning a metal surface which comprises contacting the metal surface with an inhibited aqueous alkaline cleaning solution having a pH in the range of 7 to about 10 and containing from about 0.5 to about 40 percent by weight of metal complexing agent selected from the group consisting of aminopolycarboxylic acid and hydroxypolycarboxylic acid and from about 0.005 to about 0.1 percent by weight of an inhibitor selected from the group consisting of:

(1) $A-S_x-[CH_2CH(R)NH]_n-R_1$, wherein A is hydrogen, lower alkyl, or $R_2-NH-(CH_2)_m-$ wherein R_2 is hydrogen or lower alkyl and m is an integer in the range of 1 to 8 inclusive, x is one or two, R is hydrogen or lower alkyl, n is an integer in the range of 1 to 8 inclusive and R_1 is hydrogen or lower alkyl;

(2) hydrosulfide salt of said

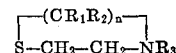


(3)



wherein R_1 , R_2 and R_3 are each hydrogen or lower alkyl and n is 1, 2, or 3;

(4) hydrosulfide salt of said



and

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(5) a mixture of at least two of such inhibitors in combination.

8. The method as in claim 7 in which the inhibitor is a compound selected from the group consisting of polyalkyleneamine sulfide, polyalkyleneamine disulfide, polyalkyleneamine mercaptan, hydroxyalkylpolyalkyleneamine sulfide, polyalkylenepolyamine sulfide, polyalkylene-
polyamine disulfide, polyalkylenepolyamine mercaptan and mixtures thereof.

9. The method as in claim 7 in which the inhibitor is bis(2-aminoethyl)sulfide.

10. The method as in claim 7 in which the concentration of the inhibitor is in the range of 0.01 to 0.5 percent by weight.

11. The method as in claim 7 in which the concentration of the inhibitor is in the range of about 0.02 to about 0.2 percent by weight.

12. The method as in claim 7 in which the cleaning solution is maintained at a temperature in the range of about 100° to 200° C. throughout the cleaning operation.

13. The method as in claim 7 in which there is also added to the cleaning solution from about 0.01 to about 0.2 percent by weight of the product of the reaction of (1) one mole of an ammonia derivative having at least one hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen, (2) from 1.5 to 10 moles of a ketone having at least one hydrogen atom on the carbon atom adjacent

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to the carbonyl group, (3) from 2 to 10 moles of an aldehyde selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and (4) from 0.6 to 24 parts by weight based on (1), (2), and (3) of a fatty acid having from 1 to 20 carbon atoms at a temperature of from about 150° F. to about 250° F. for from about 1 to 16 hours.

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