

PATENT SPECIFICATION

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NO DRAWINGS

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(54) CLEANING SOLUTIONS AND METHOD OF CLEANING METALS

(71) We, THE DOW CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, 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:—

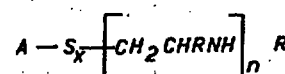
The invention relates to a method of removing iron oxides and hardness deposits from metal surfaces and to aqueous alkaline solutions containing ammonium or amine polycarboxylate chelating or complexing agents.

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 herein-after 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. 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.

According to the present invention, there is provided an aqueous solution suitable for cleaning metal surfaces which has a pH of 7 to 10 and contains 0.5 to 40 weight percent of an ammonium or amine polycarboxylic metal complexing agent and 0.01 to 0.5 weight

per cent of at least one thioethylamine of formula I

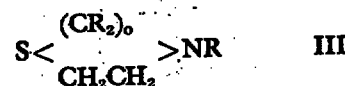


I

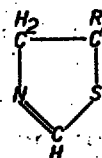
wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II



wherein R' is hydrogen or a 1 to 5 carbon alkyl group, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8 and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is 1 or 2, R is hydrogen, m is 2 and n is 1, or, x is 1, R is H, m is 2 and n is 2 or a thioethylamine of formula III



wherein R each independently is as above defined and o is 1, 2 or 3 or a thioethylamine of formula IV



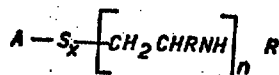
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IV

wherein both R groups are hydrogen or methyl groups respectively, or the thioethylamine of formula V



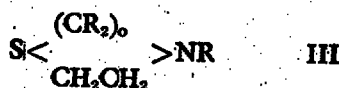
- According to a further aspect of the invention, there is provided a process for cleaning metal surfaces which comprises contacting the surfaces with an aqueous alkaline solution containing a polycarboxylate metal complexing agent and at least one thioethylamine of the formula I



- 10 wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II



- 15 wherein R' is hydrogen or a 1 to 5 carbon alkyl group, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8 and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is 1 or 2, R is hydrogen, m is 2 and n is 1, or, 20 x is 1, R is H, m is 2 and n is 2, or a thioethylamine of formula III



- 25 wherein R each independently is as above defined and o is 1, 2 or 3, or a thioethylamine of formula IV



- 30 wherein both R groups are hydrogen or methyl groups respectively, or the thioethylamine of formula V



- 85 wherein n may be 1, 2, 3 or 4, and m may be 0, 1, 2, 3, or 4, one or 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. Suitable examples of

and then rinsing the surface with water. The aqueous alkaline solution employed in the process of the invention preferably has a pH of from 7 to 10 and preferably contains from 0.01 to 0.5 weight per cent of the thioethylamine.

It is particularly advantageous for the solution to contain bis-(2-aminoethyl sulfide). It may also be desirable for the solution to contain from 0.01 to 0.20 and preferably from 0.03 to 0.15 weight percent of an amine-ketone-aldehyde-fatty acid adduct which may be obtained by 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. Use of the combination of the thioethyl amine or 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.

The invention, therefore, concerns the novel solutions and the improved process for cleaning metal surfaces.

Suitable polycarboxylic acid chelating agents include the aminopolyacetic acids of the formula

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 ethylenimines or polyethylene-polyamines containing divalent sulfur in the molecule. They are normally prepared by the reaction of hydrogen sulfide and ethylenimine in various proportions.

Essentially, each of the thioethyl amine inhibitor compounds contains the



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 200°C. At temperatures below 60°C. the inhibitors are effective but are usually not needed. The present inhibitors are of advantage because 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 which possess the



grouping are 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 sulfides, polyalkyleneamine disulfides, polyalkyleneamine mercaptans, hydroxyalkylpolyalkyleneamine sulfides, polyalkylenepolyamine sulfides, polyalkylenepolyamine disulfides and polyalkylenepolyamine mercaptans. Each of these may be used in the hydrosulfide salt form.

The present sulfur-containing amine inhibitor having the S—C—C—N grouping may also be used in combination with the adduct obtained by the chemical combination of equimolar quantities of tall oil fatty acid, epichlorohydrin and an interlinear 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 ethylenediamine 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 interlinear 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 1 percent by weight, but more preferably at the level of 0.01 to 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 10 by addition of the requisite amount of a nitrogen base such as ammonia, an alkanolamine or other suitable amine. Examples of suitable paired combinations of alkylenepolyamine polyacetic acids with nitrogen bases are listed in the following table.

Polyacetic Acid

EDTA
EDTA
EDTA
EDTA
EDTA
EDTA
EDTA
EDTA
EDTA
ethylenediaminetetrapropionic acid
N,N-di(β-hydroxyethyl)glycine
tetramethylenediamine-N,N,N',N'-tetraacetic acid
(α-hydroxyethylimino)diacetic acid

Nitrogen Base

ammonia
ethanolamine
ethylamine
ethylenediamine
diethylenetriamine
pentaethylenhexamine
dimethylamine
trimethylamine
ethylenimine

ethanolamine
ethylenediamine

ammonia

ammonia

TABLE I

Test No.	Inhibitor	Weight Percent	*Additive, Weight Percent	Corrosive Rate, lbs./ft. ² /day	gm/cm ² /day
Control	None	—	—	0.0257	0.0125
1	**Mixture A	0.2	—	0.0014	0.0007
2	bis(2-aminoethyl)disulfide	0.2	—	0.0014	0.0007
3	beta-mercaptoethylamine	0.2	—	0.0049	0.0024
4	bis(2-aminoethyl)sulfide	0.0667	0.133	0.00053	0.00026
5	(bis-(2-aminoethyl)disulfide	0.0667	0.133	0.00070	0.00033
6	beta-mercaptoethylamine	0.0667	0.133	0.00026	0.00013
7	do	0.04	0.08	0.0035	0.00017

* 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 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.

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

Second Series of Tests

5 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) a commercial amine-ketone-aldehyde-fatty

acid adduct previously described and in the footnote to the table. 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, Weight Percent	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
Control	— *	—	0.1	0.0302	0.0147
8	bis(2-aminoethyl)sulfide	0.05	.1	.0006	0.0003
9	3-thia,6-azaotane,1,8-diamine	.0335	.067	.0101	0.0049
10	do	.0367	.0733	.0082	0.0040
11	do	.04	.08	.0034	0.0017
12	do	.05	.1	.0005	0.00025
13	Mixture B	.0335	.067	.0010	0.0005
14	do	.0367	.0733	.0007	0.00033
15	do	.04	.08	.0006	0.00029
16	H ₂ S salt of bis(2-aminoethyl)sulfide	.0335	.067	.0006	0.00029
17	do	.0367	.0733	.0006	0.00029
18	do	.04	.08	.0013	0.00063
19	do	.05	.1	.0009	0.00044
20	Mixture C	.05	.1	.0004	0.00020

TABLE II (Continued)

Test No.	Inhibitor	Weight Percent	*Additive, Weight Percent	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
21	Mixture D	.05	.1	.0011	0.00054
22	Mixture E	.05	.1	.0005	0.00024
23	2-(aminoethylthio)ethanol	.067	.0335	.0548	0.0267
24	do	.0733	.0367	.0278	0.0135
25	do	.08	.04	.0034	0.00166
26	do	.1	.05	.0342	0.00167

* 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.

a — 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.

TABLE III					
Test No.	Inhibitor	Weight Percent	*Additive, Weight Percent	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
Control	—	—	—	0.2730	0.133
Control	— a	—	0.1	.0316	0.0154
27	bis(2-aminoethyl)	0.05	.1	.0019	0.00093
28	do	.04	.08	.0018	0.00088
29	thiazolidine	.05	.1	.0701	0.0342
30	bis(2-aminoethyl)sulfide	.04	.08	.0143	0.0070
31	do	.05	.1	.0038	0.00185
32	3-thia,6-azaoctane,1,8-diamine	.05	.1	.0015	0.00073
33	Mixture B	.066	.134	.0019	0.00093
34	do	.05	.1	.0014	0.00068
35	do	.04	.08	.0010	0.00049
36	do	.0366	.0733	.0006	0.00029
37	H ₂ S salt of bis(2-aminoethyl)sulfide	.0366	.0733	.0020	0.00098
38	do	.05	.1	.0016	0.00078
39	Mixture C	.04	.08	.0031	0.00151

TABLE III (Continued)

Test No.	Inhibitor	Weight Percent	*Additive, Weight Percent	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
40	Mixture C	.05	.1	.0008	0.00039
41	Mixture D	.04	.08	.0393	0.0194
42	do	.05	.1	.0017	0.00083
43	Mixture E	.04	.08	.0025	0.00122
44	do	.05	.1	.0009	0.00044
45	bis(2-aminoethyl)sulfide	.08	.04	.0147	0.00717
46	do	.1	.05	.0507	0.0247

* 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.

* — 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

5 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 comparison using (1) no inhibitor and (2) the amine-ketone-aldehyde-fatty acid adduct hereinbefore described. The results of the control tests are also summarized in Table IV. 15

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. 20

TABLE IV
Protection of Copper

Test No.	Inhibitor	Weight Percent	*Additive, Weight Percent	Temp. °C.	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
Control	—	—	—	150	0.0208	0.0102
Control	— ^a	—	0.1	150	.0204	0.0099
47	bis(2-aminoethyl)sulfide (crude)	.05	.1	150	.0034	0.00166
48	bis(2-aminoethyl)sulfide	.05	.1	150	.0008	0.00039
49	Mixture C	.05	.1	150	.0018	0.00088
50	Mixture D	.05	.1	150	.0008	0.00039
Control	—	—	—	155	.0221	0.0108
51	bis(2-aminoethyl)sulfide	.05	.1	155	.0007	0.00034
52	Mixture C	.05	.1	155	.0006	0.00029
53	Mixture E	.05	.1	155	.0005	0.00024

* Additive is the product of reaction of Rosin Amine D, tall oil fatty acids, acetophenone, and para-formaldehyde 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.

^a — 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-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 H₂S salt of bis(2-aminoethyl)sulfide and 10.0 percent of 3-thia,6-azaoctane,1,8-diamine.

Fourth Series of Tests

5 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 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. 10

TABLE V

Test No.	Bis(2-aminoethyl)Sulfide Weight, Percent	Temp. °C.	Corrosion Rate lbs./ft. ² /day	gm/cm ² /day
54	0.01	115	0.0068	0.0033
55	.02	115	.00009	0.000044
56	.05	115	.0051	0.0025
57	.02	128	.0053	0.0026
58	.05	138	.0266	0.01297

Fifth Series of Tests

15 A fifth series of tests was carried out in the same manner as the fourth series except that an intralinear 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 composi-

tion of the invention. The adducts used and the concentration thereof, the concentration of bis(2-aminoethyl)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. 20 25

Test No.	Adduct Used	Weight Percent	Weight Percent bis(2-aminoethyl)-sulfide	Corrosion Rate, lbs./ft. ² /day (gm/cm ² /day)		
				169°C.	137°C.	^a 130°C.
59	Adduct A	0.005	0.02	0.0096(0.0047)	0.0045(0.0022)	—
60	do	.002	.02	^b 0.0097(0.00473)	.0032(0.00156)	^b 0.0029(0.0014)
61	do	.002	.05	—	.0045(0.0022)	—
62	do	.02	.02	—	—	.0075(0.00366)
63	Adduct B	.005	.02	.0100(0.00488)	.0052(0.00254)	—
64	do	.002	.02	.0097(0.00475)	.0042(0.00204)	—
65	do	.02	.02	—	—	.0080(0.0039)
66	—	—	.05	.0443(0.0216)	.0214(0.01044)	—

^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

5 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 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	gm/cm ² /day
67	Adduct A	0.02	130	* 0.0038	0.00185
68	do	.002	132	.0033	0.0016
69	do	.002	130	* .0035	0.0017
70	do	.002	120	* .0056	0.0027
71	Adduct B	.02	120	—	

* = 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

5 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

25 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

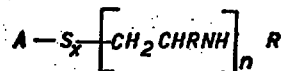
first boiler also contains 0.002 percent by weight of the adduct of tall oil fatty acids, epichlorohydrin and triethylenetetramine. The solution in the first boiler contains EDTA as the polycarboxylic acid complexing agent and the solution has an initial pH of 9 obtained by the addition of the requisite 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.

WHAT WE CLAIM IS:—

1. An aqueous solution suitable for cleaning metal surfaces which has a pH of 7 to 10 and contains 0.5 to 40 weight per cent of an ammonium or amine polycarboxylate metal complexing agent and 0.01 to 0.5 weight per cent of at least one thioethylamine of formula I



I

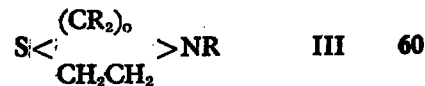
wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II



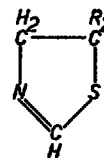
II

wherein R' is hydrogen or a 1 to 5 carbon alkyl group, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8 and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is

1 or 2, R is hydrogen, m is 2 and n is 1, or, x is 1, R is H, m is 2 and n is 2 or a thioethylamine of formula III



wherein R each independently is as above defined and o is 1, 2 or 3, or a thioethylamine of formula IV



IV

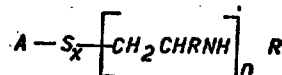
wherein both R groups are hydrogen or methyl groups respectively, or the thioethylamine of formula V



2. An aqueous solution as claimed in claim 1 the thioethylamine of which is bis(2-aminoethyl)sulfide.

3. An aqueous solution as claimed in claims 1 or 2 containing in addition 0.01 to 0.20 weight per cent of an amine-ketone-aldehyde-fatty acid adduct as hereinbefore described.

4. A process for cleaning metal surfaces which comprises contacting the surfaces with an aqueous alkaline solution containing a polycarboxylate metal complexing agent and at least one thioethylamine of the formula I



I

wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II



II

wherein R' is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is 1 or 2, R is hydrogen, m is 2 and n is 1, or x is 1, R is H, m is 2 and n is 2 or a thioethylamine of formula III





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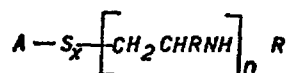
first boiler also contains 0.002 percent by weight of the adduct of tall oil fatty acids, epichlorohydrin and triethylenetetramine. The solution in the first boiler contains EDTA as the polycarboxylic acid complexing agent and the solution has an initial pH of 9 obtained by the addition of the requisite 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.

WHAT WE CLAIM IS:—

1. An aqueous solution suitable for cleaning metal surfaces which has a pH of 7 to 10 and contains 0.5 to 40 weight per cent of an ammonium or amine polycarboxylate, metal complexing agent and 0.01 to 0.5 weight per cent of at least one thioethylamine of formula I



I

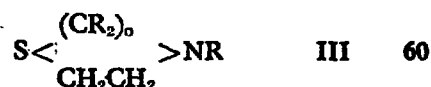
wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II



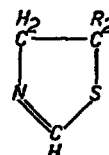
II

wherein R' is hydrogen or a 1 to 5 carbon alkyl group, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8 and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is

1 or 2, R is hydrogen, m is 2 and n is 1, or, x is 1, R is H, m is 2 and n is 2 or a thioethylamine of formula III



wherein R each independently is as above defined and o is 1, 2 or 3, or a thioethylamine of formula IV



IV

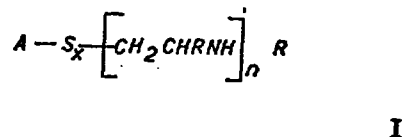
wherein both R groups are hydrogen or methyl groups respectively, or the thioethylamine of formula V



2. An aqueous solution as claimed in claim 1 the thioethylamine of which is bis(2-aminoethyl)sulfide.

3. An aqueous solution as claimed in claims 1 or 2 containing in addition 0.01 to 0.20 weight per cent of an amine-ketone-aldehyde-fatty acid adduct as hereinbefore described.

4. A process for cleaning metal surfaces which comprises contacting the surfaces with an aqueous alkaline solution containing a polycarboxylate metal complexing agent and at least one thioethylamine of the formula I

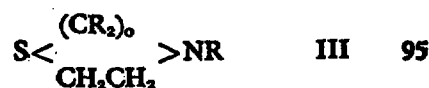


wherein A is hydrogen, a 1 to 5 carbon alkyl group or a radical of formula II

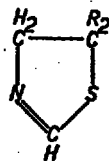


II

wherein R' is hydrogen or a 1 to 5 carbon alkyl group, m is 1 to 8, x is 1 or 2, R each independently is hydrogen or a 1 to 5 carbon alkyl group and n is 1 to 8, or the hydro-sulfide salt thereof with the restriction that when the radical of formula II is incorporated in formula I and R' is hydrogen either x is 1 or 2, R is hydrogen, m is 2 and n is 1, or x is 1, R is H, m is 2 and n is 2 or a thioethylamine of formula III



wherein R each independently is as above defined and o is 1, 2 or 3, or a thioethylamine of formula IV



IV

- 5 wherein both R groups are hydrogen or methyl groups respectively, or the thioethylamine of formula V



- 10 and then rinsing the surface with water.
5. A process as claimed in claim 4 wherein the aqueous alkaline solution employed has a pH of from 7 to 10.
6. A process as claimed in claims 4 or 5 wherein the aqueous alkaline solution employed

contains from 0.01 to 0.5 weight per cent of the thioethylamine. 15

7. A process as claimed in claim 6 wherein the aqueous alkaline solution employed contains 0.02 to 0.20 weight of the thioethylamine.

8. A process as claimed in any of claims 4 to 7 wherein the aqueous alkaline solution employed contains bis(2-aminoethyl)sulfide. 20

9. A process as claimed in any of claims 4 to 8 wherein the aqueous alkaline solution employed also contains 0.01 to 0.2 weight per cent of an amine-ketone-aldehyde-fatty acid adduct as hereinbefore described. 25

10. A process as claimed in claim 4 for cleaning metal surfaces substantially as hereinbefore described with reference to the specific examples. 30

11. Metal cleaning solutions as claimed in claim 1 substantially as hereinbefore described with reference to the specific examples.

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