

1

3,481,882

CLEANING COMPOSITION AND METHOD OF CLEANING ARTICLES THEREWITH

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9 Claims

ABSTRACT OF THE DISCLOSURE

A cleaning composition for removing foreign matter from metal surfaces which contains a water soluble acid, a selected thiourea or thioamide and a selected anionic surface active agent, and a process for cleaning metal surfaces using the identified cleaning composition.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 438,613, filed Mar. 10, 1965 now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new and improved acid cleaning compositions for removing foreign matter, including coatings, from metal articles and to a method for cleaning and passivating the surfaces of such articles.

Description of the prior art

Acid pickling compositions for cleaning and derusting steel have long been used in the treatment of steel preparatory to electroplating, galvanizing, or other process for coating of steel. Previously known acid baths for the cleaning and derusting of steel cause objectionable corrosion and pitting of steel surfaces and even when thoroughly rinsed from the steel, the latter is subject to rapid re-rusting whereby such steel may contain a considerable quantity of soluble iron compounds, e.g., iron oxides or iron hydroxides.

The careful cleaning and derusting of steel is of particular importance as a step preceding halogen-tin electroplating of steel. Not only must the steel surface be free of rust and pits, but the presence of material amounts of soluble iron compounds promotes the formation and precipitation of sodium stannifluoride (Na_2SnF_6) in tin plating baths of the type described by Schweikher in U.S. Patent 2,407,579. The presence of precipitated sodium stannifluoride necessitates the frequent filtration of the plating bath and the loss of costly tin and fluoride.

The cleaning of steel preparatory to tin plating by the halogen-tin plating process presents a further problem in that the cleaning and tin plating are carried out continuously at a speed of up to 2000 feet per minute. Therefore, in a 100-ft. cleaning bath, there is an immersion time of only three seconds within which to clean and derust the steel. Moreover, in such plating operation it is necessary at times to stop or slow down the strip to permit machinery adjustments or joining of sheets to each other. At such stops, the strip may be in contact with the acid cleaning solution for periods of several minutes, e.g., up to 30 minutes. Provision must be made to lift the strip out of the solution or the acid must be drained to prevent dissolution and consequent rupture of the sheet.

In addition to cleaning the surfaces of steel to remove rust, removal of surface coatings, such as phosphate

2

coatings formed in organic solvents of the type described in Copelin U.S. Patent 2,789,070, or formed in aqueous solutions may be necessary. At the present time, a prolonged treatment in an acid bath, using elevated temperatures is required. In addition, problems have been experienced with sludge build up in phosphatizing units and an efficient cleaning composition would be highly desirable. The surfaces of metals other than mild steel also require cleaning. It is desirable to have a treating solution which may be used on iron alloys, e.g., stainless steel and cast iron, as well as copper, brass and lead-tin solder.

SUMMARY

The principal object of this invention is to provide a composition and process for the treatment of ferrous metals in which both hydrogen evolution corrosion and ferric ion corrosion is inhibited.

It is another object of this invention to provide a composition and process for cleaning the surface of copper and copper alloy articles.

Still another object of this invention is to provide a composition which will remove phosphate coatings from steel surfaces.

A further object of this invention is to provide a composition for cleaning and derusting steel articles and for preventing after-rusting following acid cleaning and retarding subsequent rerusting after drying.

Other objects of the invention will be apparent from the following description.

The objects of this invention are accomplished by providing aqueous treating compositions containing as essential ingredients from about 1% to about 30% by weight of an inorganic or organic water-soluble acid, preferably an acid having a solubility in water of at least about 10 grams per 100 ml., 0.025 gram per liter to saturation of selected thiourea and thioamide compounds, and 0.01 to 3.5 grams per liter of certain anionic surface active agents. The metal article to be treated is either washed with or immersed in the treating solution for a controlled period of time, e.g., a few seconds to an hour or more depending on the condition of the surface of the article, concentration of ingredients in the solution and temperature of the solution, after which it is rinsed with an alkaline solution, e.g., sodium hydroxide, rinsed with water and dried.

BRIEF DESCRIPTION OF THE DRAWING

The figure of the drawing, which will be discussed in detail later herein, graphically illustrates operability of cleaning compositions which are prepared according to the present invention and compositions from which one of the essential ingredients of the compositions of this invention is omitted. The area under the solid line defines a zone of operability for selected compositions within the scope of the present invention. The area under the broken line defines a very limited area of operability when an essential ingredient is omitted.

DESCRIPTION OF THE INVENTION

As mentioned previously, the essential ingredients of the treating solution of this invention include a thiourea or a thioamide. While the just-mentioned compounds, described in detail later herein, are effective to a limited degree in inhibiting hydrogen evolution corrosion as well as ferric ion corrosion of metals when used alone in an acid medium, I have discovered that when these materials are used in combination with an anionic surface active agent, the effect on corrosion inhibition is not merely additive but a synergistic action takes place. This is particularly surprising in view of my findings that addition of anionic surface active agents to known corrosion inhibitors which are commercially available has little, if

3

any, effect in inhibiting corrosion and in some cases actually increases the corrosion problem.

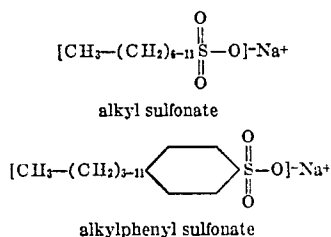
The thioureas which are useful in this invention are those having the formula



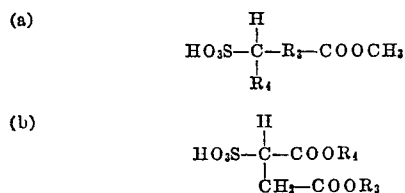
where R and R' are selected from the group consisting of alkyl radicals having a chain length of from 4 to 6 carbon atoms and phenyl and tolyl radicals. Representative compounds include alkyl thioureas such as 1,3-dibutylthiourea, N,N'-dihexylthiourea, N,N'-hexylbutylthiourea, N,N'-2-methyl-hexylpentylthiourea, aryl and alkyl substituted aryl thiourea such as 1,3-diphenylthiourea, diorthotolylthiourea and 1,3-tolylphenylthiourea. The aryl thioureas may have the alkyl substitution in the ortho, meta or para positions.

The thioamides may be selected from the group consisting of N-butylthiobutyramide, isobutylthioacetamide, N,N'-ethylene bithiobenzamide, N-phenylthiobenzamide, and N-isobutylthiobenzamide. These inhibitors, which are solids, may be added to the bath in powdered form. The compounds are sparingly soluble in the bath and are added in an amount from 0.025 gram per liter to the saturation point. By prolonged exposure in the bath, more than 0.625 gram per liter may be dissolved. Preferably, from 0.1 to 0.3 gram per liter is used. A continuous supply of the inhibitor in the cleaning composition may be conveniently provided by compacting or otherwise consolidating the inhibitor powder into pellets or bricks for immersion in the acid solution. Alternatively, pellets may be placed into loosely woven bags to protect them in solutions which are subject to vigorous agitation such as in a tin plating line.

As mentioned previously, the reduction of corrosion is greatly enhanced by addition of certain anionic surface active agents. These agents, which are added in an amount from 0.01 to 3.5 grams per liter, preferably one gram or less, have been found to reduce corrosion by as much as a factor of 8. The long chain alkyl alkali metal and amine sulfonates in which the alkyl chain has a length of from 7 to 12 carbon atoms and alkylphenyl alkali metal and amine sulfonates in which the alkyl chain has a length of from 4 to 12 carbon atoms are useful. The carbon chains may be straight or branched. The saturated hydrocarbon sodium and potassium sulfonates which contain mixtures of aliphatic and cycloaliphatic groups, such as those based on white oils, may also be used. Illustrative preferred compositions include those having the formulas:



Certain sulfonated esters of mono- and di-basic carboxylic acids containing straight or branched alkyl groups having a branched or straight chain length of 5 to 9 carbon atoms are also useful. Typical compositions have the formulas



wherein R₃ and R₄ contain from 5 to 9 carbon atoms.

The anionic surface active agents which are preferred

4

are among the many commercially available compositions described in publications, such as McCutcheon, John W., "Synthetic Detergents," MacNair-Dorland Company, New York, 1950, and Schwartz, Anthony M., Perry, James W., and Berch, Julian, "Surface Active Agents and Detergents," Interscience Publishers, Inc., New York, 1958.

In the foregoing discussion relating to the thiourea, thioamide and surface active compounds, the length of the carbon chain of the alkyl radicals is determined in the conventional manner. The chain may be straight or branched. The length of these chains rather than the total number of carbon atoms contained therein, has been found to be determinative of the suitability of the compounds for use in accordance with the present invention. For example, the alkyl radicals may contain methyl, ethyl, propyl or butyl substituents provided that the specified chain length is not exceeded.

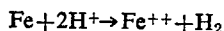
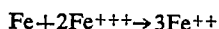
A wide variety of acids may be used. The particular acid or acids selected will depend on such factors as the condition of the surface to be treated, the particular metal being treated, and the strength of the acid. The acid should, of course, be free from substituents which might react with the other components of the solution to form undesirable precipitates. In general, any of the simple mineral and organic acids having a solubility in water at room temperature of at least about 10 grams per 100 ml. are useful. More than one acid may be used. For example, a preferred solution for treating steel includes both an organic and an inorganic acid. From 0.75% to 18% oxalic acid (preferably 5-10%) which is known to be an effective solvent for rust, and from 3% to 15% of sulfuric acid (preferably 4-12%) which is a solvent for ferrous oxalate, may be used. Coatings of ferrous oxalate are formed readily on steel in solutions of oxalic acid containing dissolved iron. Therefore, in order to prevent formation of coatings of ferrous oxalate on the metal, it is necessary to use oxalic and sulfuric acid in certain ratios. The preferred ratio will depend on such factors as temperature of the solution and the concentration of dissolved iron (in the ferric state) present in the solution.

The optimum concentrations of the acid will, of course, vary depending on the strength of the particular acid or acids used as well as the material being treated and the temperature of treatment.

Further in this regard reference is made to the figure of the drawing which graphically illustrates a range of concentrations of oxalic acid and sulfuric acid using a treating composition which has an accumulated ferric ion content (2.2 grams per liter of iron in the ferric state) to simulate dissolved iron oxides, i.e., rust, which has been removed from a treated metal surface. The area below the solid line on the graph defines a zone in which the depicted proportions of the two acids are effective when a treating composition which includes a surface active agent in an amount within the previously mentioned limits is used to clean the surface of a low carbon steel sheet. In contrast, the restricted area below the broken line defines the very limited zone of operability when the surface active agent is omitted from the composition. For example, at 6% sulfuric acid, only 2% oxalic acid can be used when the surface active agent is omitted whereas with the surface active agent a much stronger solution, i.e., up to 15% of oxalic acid may be used. In preparing the graph of the figure a treating temperature of 160° F. was used with the treating solution containing 0.1 g./l. of diorthotolylthiourea, 10 g./l. ferric sulfate (22% Fe) to simulate build-up of corrosion product and dissolved rust, and 0.1 g./l. of sodium dodecylbenzene sulfonate as the surface active agent. The treating time was 30 minutes. As a general rule, temperatures above about 180° F. should be avoided with a preferred operating range being between about 130° F. to 160° F. The solid line will be moved upward at lower treating temperatures and slightly downward at higher treating temperatures.

5

In the following examples which illustrate the practice of this invention, parts and percentages are by weight unless otherwise indicated. In certain examples, ferric sulfate was added to simulate commercial conditions in which dissolved iron would accumulate and cause ferric ion corrosion in addition to hydrogen evolution corrosion, the two types of corrosion being illustrated by the following reactions in which Fe represents steel:



EXAMPLE I

A series of tests were carried out in which a low carbon, 0.01-inch thick, sheet steel was immersed for thirty minutes in a cleaning solution having the following composition:

Oxalic acid	-----percent	1.5
Sulfuric acid	-----do	5.0
Diorthotolylthiourea	-----grams per liter	0.2
"Oronite S" ¹	-----do	0.14

¹ Trade name for Oronite Chemical Company's sodium alkyl-aryl sulfonate prepared by sulfonating benzene alkylated with a tetramer of propylene and then neutralizing the sodium hydroxide.

The steel was immersed in the solution which was maintained at a temperature of 160° F. for thirty minutes. At the end of the thirty minutes, the steel was removed from the solution and found to be bright and unstained.

A series of additional experiments was conducted in which (a) 0.1 gram per liter of stannous sulfate and (b) 10 grams per liter of ferric sulfate were added to the cleaning solution. In each experiment the steel was found to be bright and clean. The weight loss was determined and the results are recorded in the following table:

6

TABLE 1

[Weight loss, g./sq. dm.]	
No Stannous Sulfate	With 0.1 g./l. SnSO ₄
Without Dissolved Iron	
0.0008	0.0115
0.0009	0.0016
0.0033	0.0012
0.0040	0.0006
0.0023	0.0004
0.0009	0.0006
0.0020 average	0.0009 average
With 10 g./l. Ferric Sulfate (22% Fe)	
0.0080	0.0139
0.0061	0.0123
0.0071	0.0125
0.0160	0.0176
0.0093 average	0.0141 average

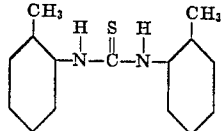
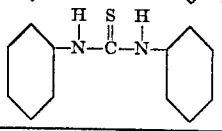
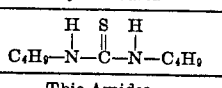
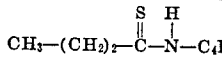
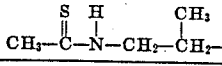
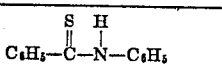
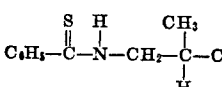
EXAMPLE II

A series of experiments were conducted in which a low carbon, can stock, 0.3 mm. thick, in sheets of 200 sq. cm., were immersed in a cleaning solution having the following composition:

Oxalic acid	-----percent	1.5
Sulfuric acid	-----do	5.0
Stannous sulfate	-----grams per liter	0.2
Sodium dodecylbenzene sulfonate	-----do	0.2

Various inhibitors were added in an amount of 0.1 gram per liter to the solution samples. The samples, can stock sheets, were immersed in the solution which was held at 160° F. for a period of thirty minutes, after which they were removed and the weight loss was determined. The sheets were found to be bright and free from stains. The results are set forth in the table which follows:

TABLE 2

Compound	Structure	Weight Loss, * g./sq. dm.	
		No Iron	With Iron (2.2 g./l. Fe ⁺⁺⁺)
None (Wetting Agent Only)		0.0241	0.2184
Aryl Thioureas			
Diorthotolylthiourea		0.0011	0.0261
1,3-diphenylthiourea (thiocarbamilide)		0.0014	0.0231
Alkyl Thiourea			
1,3-dibutylthiourea		0.0013	0.0368
Thio Amides			
N-butylthiobutyramide		0.0017	0.0409
Isobutylthioacetamide		0.0025	0.0331
Aryl Thioamides			
N-phenylthiobenzamide		0.0005	0.0305
N-isobutylthiobenzamide		0.0022	0.0170

*Average of 2 or more tests.

The effectiveness of the ingredients in reducing weight loss is clearly demonstrated from the data in the foregoing table. Without the surface active agents the weight loss was high and the surface finish was destroyed by corrosion. The surface remained bright and free of corrosion when the surface active agent was used.

EXAMPLE III

Sheets of low carbon steel, 0.01 inch thick and 10 cm. square, were immersed for thirty minutes in a cleaning solution held at 160° F. having the following composition:

Water	ml.	900
Sulfuric acid (96%)	ml.	27.1
Oxalic acid	grams.	14.4
Stannous sulfate	do.	0.18
Diorthotolylthiourea	do.	0.18
Anionic surface active agent (See Table 3 which follows.)	do.	0.2
Ferric sulfate (22% Fe)	do.	10

To separate samples of the solution, various anionic surface active agents were added. The agents and the

periments, low carbon, sheet steel coupons, 10 cm. square, were immersed in cleaning solutions, having the following compositions, for thirty minutes at a temperature of 160° F.

5	Water	ml.	900
	96% sulfuric acid (5% by weight)	ml.	27.1
	Oxalic acid (1.5% by weight)	grams.	14.4

The combinations of ingredients and the weight loss suffered by the coupons are indicated in Table 4 which follows. From these data it will be apparent that diorthotolylthiourea effectively reduces both hydrogen evolution and ferric ion corrosion. The surface active agents, while having no significant effect on corrosion inhibition when used alone, greatly enhance the action of the diorthotolylthiourea in reducing both of the aforementioned types of corrosion. In addition these agents suppress formation of iron oxalate coatings on steel and promote rinsability. It will be noted that the stannous sulfate is effective in decreasing corrosion especially in solutions having a low concentration of ferric ions. Its use is recommended since in most cases accumulation of dissolved iron will be slow.

TABLE 4

Solution		Weight Loss (g./sq. dm.)	Surface Appearance
A	(1) 5% sulfuric acid plus 1.5% oxalic acids	0.2689	Dull.
	(2) No. 1 plus 10 g. ferric sulfate (22% Fe)	0.3944	Do.
	(3) No. 2 plus 0.18 g. diorthotolylthiourea	0.0608	Do.
	(4) No. 3 plus 0.18 g. stannous sulfate	0.0557	Do.
	(5) No. 4 plus 0.18 g. sodium dodecylbenzene sulfonate	0.0115	Bright.
B	(1) 5% sulfuric plus 1.5% oxalic acids	0.2789	Dull.
	(2) No. 1 plus 0.18 g. diorthotolylthiourea	0.0040	Bright.
	(3) No. 2 plus 10 g. ferric sulfate	0.0782	Dull.
	(4) No. 3 plus 0.18 g. stannous sulfate	0.0582	Do.
	(5) No. 4 plus 0.18 g. sodium dodecylbenzene sulfonate	0.0120	Bright.
C	(1) 5% sulfuric plus 1.5% oxalic acids plus 10 g. ferric sulfate plus 0.18 g. diorthotolylthiourea	0.0995	Dull.
	(2) No. 1 plus 0.18 g. stannous sulfate	0.0762	Do.
	(3) No. 2 plus 0.18 g. "Oronite S"	0.0076	Bright.
D	(1) 5% sulfuric plus 1.5% oxalic acids	0.2507	Dull.
	(2) No. 1 plus 0.18 g./l. sodium dodecylbenzene sulfonate	0.1773	Do.
	(3) No. 2 plus 0.18 g./l. diorthotolylthiourea	0.0032	Bright.
	(4) No. 3 plus 0.2 g./l. stannous sulfate	0.0011	Do.
E	(1) 5% sulfuric plus 1.5% oxalic acids plus 10 g./l. ferric sulfate	0.4309	Dull.
	(2) No. 1 plus 0.18 g./l. sodium dodecylbenzene sulfonate	0.4368	Do.
	(3) No. 2 plus 0.18 g./l. diorthotolylthiourea	0.0348	Bright.
	(4) No. 3 plus 0.2 g./l. stannous sulfate	0.0213	Do.

weight loss, which was determined on the bright, clean samples, are recorded in the table which follows:

TABLE 3

Anionic Surface Active Agent (Trade Name)	Description ¹	Weight Loss ² (g./sq. dm.)
None		0.1011
"Oronite S" (Oronite Chem. Co.)	Sodium alkyl aryl sulfonate	0.0092
"Ultrawet 35KX" (Atlantic Ref. Co.)	Alkyl benzene sodium sulfonate	0.0088
"Santomerse No. 43" (Monsanto)	Amine salt of alkyl aryl sulfonate	0.0206
"Ahcowet-RS Anhydrous" (Arnold Hoffman Co.)	Sulfonated fatty acid ester	0.0130
"Ahcowet-RS" (Arnold Hoffman Co.)	Organic solvent solution of sulfonated fatty acid	0.0235
"Aerosol OT" (American Cyanamid Co.)	Diocetyl ester of sodium sulfosuccinic acid	0.0184

¹ Taken from "Detergents and Emulsifiers Up-to-Date" by John W. McCutcheon, 1962.

² Average of two or more tests.

From the data set forth in the table it can be seen that the presence of the anionic surface active agent significantly reduces the weight loss in the cleaning solution. By comparing the data in Table 3 with that in Table 2, the synergistic action which occurs by virtue of the presence of the inhibitor in conjunction with the surface active agent is evidenced.

EXAMPLE IV

This example illustrates the synergistic action of the surface active agent when used in combination with an inhibitor in oxalic and sulfuric acids. In a series of ex-

EXAMPLE V

The following example shows that corrosion is essen-

tially independent of acid concentration in solutions of the present invention. Low carbon steel sheets were immersed for thirty minutes in a cleaning solution having the following composition:

Oxalic acid and sulfuric acid
(As shown in Table 5 which follows.)

0.1 g./l. diorthotolylthiourea
0.2 g./l. alkylaryl sodium sulfonate ("Oronite S")
10 g./l. ferric sulfate (22% Fe) when shown.

TABLE 5

Solution (Weight Percent)	Weight Loss (g./sq. dm.)		
	Sulfuric Acid, Percent	Without Iron	With Iron
Oxalic Acid, Percent			
160° F.:			
0.75.....	3	0.0008	0.0021
0.75.....	3	0.0010	0.0220
1.5.....	6	0.0006	0.0276
3.0.....	12	0.0010	0.0231
140° F.:			
0.75.....	3	0.0006	0.0172
1.5.....	6	0.0003	0.0067
3.0.....	12	0.0007	0.0071

EXAMPLE VI

The effect of the anionic surface active agent on weight loss of low carbon steel sheets using various acid ratios is illustrated by this example in which the cleaning solution had the following composition. A temperature of 160° F. and treating time of thirty minutes were used. These data show that the presence of the surface active agent there is very little increase in weight loss as the total concentration of acid is increased from 9 to 27%,

Oxalic and sulfuric acids

(In concentrations indicated in Table 6, which follows.)

0.1 g./l. diorthotolylthiourea

0.1 g./l. stannous sulfate

Wetting agent when used:

0.14 g./l. alkylaryl sodium sulfonate

("Oronite S")

TABLE 6

Solution (Percent by Weight)	Weight Loss (g./sq. dm.)	
	No Wetting Agent	With Wetting Agent
3% Sulfuric Acid:		
0.5% oxalic acid.....	0.0910	-----
0.75% oxalic acid.....	0.1043	-----
5.0% oxalic acid.....	-----	0.0074
6.0% oxalic acid.....	-----	0.0146
10.0% oxalic acid.....	-----	0.0136
6% Sulfuric Acid:		
1.0% oxalic acid.....	0.0332	-----
2.0% oxalic acid.....	0.0850	-----
13.0% oxalic acid.....	-----	0.0147
16.0% oxalic acid.....	-----	0.0093
9% Sulfuric Acid:		
1.75% oxalic acid.....	0.1097	-----
2.5% oxalic acid.....	0.1104	-----
3.0% oxalic acid.....	0.0824	-----
9.0% oxalic acid.....	-----	0.0213
18.0% oxalic acid.....	-----	0.0233

EXAMPLE VII

A low carbon steel sheet, 200 centimeters square, was immersed for 30 minutes in an aqueous solution containing as the sole additive 6% by weight of hydrochloric acid at a temperature of 160° F. The sample was weighed before and after treatment and found to have lost 1.5 grams per sq. dm.

In separate experiments, solutions were prepared containing 6% hydrochloric acid and 0.2 gram per liter of each of the ingredients as listed in Table 7 which follows. Weight loss is reported in grams per sq. dm.

TABLE 7

Inhibitor	Weight Loss with Inhibitor Only	Weight Loss with Inhibitor and Surface Active Agent ¹
Diorthotolylthiourea.....	0.0308	0.0086
Kontol 121 ²	0.0546	0.1085
Primonox No. 10 ³	0.0351	0.3039
Polyrad 98 ⁴	0.0176	0.0328
Dowell (A30W).....	0.0158	0.0812

¹ Sodium dodecylbenzene sulfonate.

² Trade name of Tretolite Division, Petrolite Corp. for its corrosion preventive reagent.

³ Trade name for Rohm & Haas Company's tertiary alkylamino-polyether alcohol.

⁴ Trade name for Hercules Chemical Company's Rosin Amine D ethylene oxide derivatives.

From the data reported, it will be readily apparent that when using one of the inhibitors of this invention, diorthotolylthiourea, in combination with the surface active agent, a marked reduction in weight loss results. In contrast, when using the commercially available compounds which are sold as corrosion preventive agents, addition of the surface active agent resulted in increased rather than reduced weight loss.

EXAMPLE VIII

This example illustrates the use of treating solutions of this invention in cleaning surfaces of metals other than mild steel. An aqueous solution containing 10% by weight of hydrochloric acid and 0.2 gram per liter of each of the ingredients as indicated in Table 8 which follows. Ferric chloride, added as FeCl₃·6H₂O, was included in the amount of 10 grams per liter to simulate a solution previously used in treating steel. The metal samples were weighed before treatment and after treatment in the solution for 30 minutes at 160° F. Weight loss is reported in grams per sq. dm.

TABLE 8

Copper sheet

	Weight loss
Acid alone.....	0.0895
Acid plus diorthotolylthiourea.....	0.0755
Acid plus diorthotolylthiourea and sodium dodecylbenzene sulfonate.....	0.0070

Brass sheet (70% Cu-30% Zn)

	Weight loss
Acid alone.....	0.0710
Acid plus diorthotolylthiourea.....	0.0325
Acid plus diorthotolylthiourea and sodium dodecylbenzene sulfonate.....	0.0062

AISI 304 stainless steel¹ (sulfamic acid)

	Weight loss
Acid alone.....	0.1924
Acid plus diorthotolylthiourea.....	0.0197
Acid plus sodium dodecylbenzene sulfonate.....	0.1584
Acid plus diorthotolylthiourea and sodium dodecylbenzene sulfonate.....	0.0030

¹ 10% sulfamic acid substituted for HCl; treating time 2 hours; no FeCl₃ added.

EXAMPLE IX

This example illustrates the use of compositions of this invention in removing phosphate coatings without appreciable attack on the steel substrate as is required, e.g., in determinations of coating weight.

A weighed steel panel was given a phosphate coating of the type described in Copelin U.S. 2,789,070 and, after re-weighing, was immersed in a bath at room temperature having the following composition:

5% sulfuric acid
1.5% oxalic acid
0.2 g./l. diorthotolylthiourea
0.2 g./l. sodium dodecylbenzene sulfonate
0.2 g./l. stannous sulfate

11

After a period of five seconds, the steel panel was removed from the bath, rinsed first in a 2% NaOH solution, and then in water at room temperature. Optical examination of the panel and weighing revealed that the phosphate coating had been entirely removed with only negligible attack on the steel.

EXAMPLE X

To simulate high speed automated treatment in electroplating lines at steel mills, panels of sheet steel, 200 sq. cm. in total area were immersed in acid de-rusting solutions for 5 seconds at 160° F. To simulate dissolved iron in the acid bath, 10 g./l. of ferric sulfate was added. Upon removal from this bath the panels were either rinsed in (a) water at room temperature or in (b) a solution of 1 to 3% sodium hydroxide at room temperature and then in water at room temperature. The panels were then dried by wiping with a white towel to determine the effectiveness of the rinsing procedure in removing entrained iron and in preventing after-rusting in the rinsing solution. Traces of iron hydroxides or oxides are readily detected by discoloration of the towel.

(a) Panels rinsed only in water always contained enough adherent iron hydroxides to discolor the towel during wiping. (b) Panels rinsed in the sodium hydroxide solution before the room temperature water rinse were clear of adherent compounds of iron and did not discolor the towel. Further evidence of the removal of iron compounds from the panels during rinsing is given by the precipitation and accumulation of iron hydroxides in the alkaline solution which turns orange in color.

Upon exposure to the laboratory atmosphere the dried panels which had been given the alkaline rinse resisted rusting for about 72 hours while panels rinsed only in water and dried resisted rusting in the laboratory for only 24 hours.

EXAMPLE XI

Low carbon steel sheets 200 centimeters square were immersed for 30 minutes in aqueous solutions containing the following additives:

Solution A

789 grams H₂O
111.1 milliliters 90% formic acid
0.75 grams ferric formate

Solution B

832 grams H₂O
67.5 milliliters 85% H₃PO₄
0.74 grams Fe(PO₄)

The temperature of the solution was maintained at 160° F. In supplemental experiments, additions of sodium dodecylbenzene sulfonate and diorthotolylthiourea were made to the basic solutions. The samples were weighed before and after treatment (two samples were used in each experiment) and found to have weight losses as set forth in the following table:

TABLE 9

Additive	Weight Loss, g./sq. dm.	
	Solution A	Solution B
None.....	0.0895	0.2206
0.2 g./l. sodium dodecylbenzene sulfonate.....	0.0908	0.2193
	0.1183	0.1655
	0.1242	0.1822
	0.0079	0.0047
0.22 g./l. diorthotolylthiourea.....	0.0079	0.0053
0.2 g./l. sodium dodecylbenzene sulfonate and 0.22 g./l. diorthotolylthiourea.....	0.0056/0.0053	0.0017/0.0014

12

EXAMPLE XII

The following example illustrates the use of a composition of this invention in removing water deposits from stainless steel heat exchanger tubing. A sample of the deposit was scraped from the tubing and found by spectroscopic analysis to contain the following elements:

Element:	Percent by weight	
Iron	do	1-5
Manganese	do	5-25
Zinc	do	10-50
Silicon	do	0.5-2
Magnesium	do	0.2-1
Aluminum	do	0.5-2
Calcium	p.p.m.	500-2500
Lead	p.p.m.	200-1000
Titanium	p.p.m.	100-500
Barium	percent by weight	0.1-0.5
Sodium	p.p.m.	100-500
Chromium	p.p.m.	100-500
Nickel	parts by weight	0.5-2
Copper	p.p.m.	100-500

The stainless steel tubing was immersed for five minutes in an aqueous solution having the following composition while maintaining the composition at a temperature of 150° F.:

5% sulfuric acid
1.5% oxalic acid
0.2 g./l. diorthotolylthiourea
0.2 g./l. sodium dodecylbenzene sulfonate

The tubing was removed from the solution and inspected. The water deposit was found to have been completely removed.

EXAMPLE XIII

In the following experiments, steel sheets 200 centimeters square were immersed in aqueous solutions for 30 minutes while maintaining the solution at 160° F.

TABLE 10

Solution:	Weight Loss g./sq. dec.		
	10% Acid	20% Acid	30% Acid
Acetic			
A ¹	0.0630	0.0537
B ²	0.1565	0.1085
C ³	0.0915	0.0718
D ⁴	0.0672	0.0457
Hydroxyacetic			
A ¹	0.0215
B ²	0.1245
C ³	0.0737
D ⁴	0.0510
Citric			
A ¹	0.1307
B ²	0.1807
C ³	0.0625
D ⁴	0.0482
Sodium Bisulfate			
A ¹	0.1992	0.2997
B ²	0.2160	0.3955
C ³	0.0639	0.0516
D ⁴	0.0313	0.0232

TABLE 10—Continued

	Weight Loss g./sq. dec.		
	10% Acid	20% Acid	30% Acid
	5% Hydrochloric+5% Sulfamic		
A ¹	0.6187
B ²	0.7270
C ³	0.0493
D ⁴	0.0331
	10% Formic+10% Hydroxyacetic		
A ¹	0.0302
B ²	0.1825
C ³	0.0767
D ⁴	0.0547
	5% Sulfamic+5% Hydroxyacetic		
A ¹	0.0470
B ²	0.2015
C ³	0.0615
D ⁴	0.0434

¹ Acid only.

² Solution A plus 2.2 g/l. Fe³⁺.

³ Solution B plus 0.2 g/l. diorthotolylthiourea.

⁴ Solution C plus 0.2 g/l. sodium dodecylbenzene sulfonate.

From the foregoing data, it will be seen that while some of the acids themselves do not materially corrode the steel sample as soon as ferric ion appears in the system, the corrosion level is substantially increased. The corrosion is then controlled by the combination of essential ingredients of the present invention.

In addition to the essential ingredients which have been specifically identified herein, it will be apparent to those skilled in the art that other acids, thioamides and thioureas within the general disclosure herein are useful in the present invention. Among the many acids which are useful are sulfamic acid, formic acid, hydroxyacetic acid, sulfuric acid, hydrochloric acid, sodium bisulfate (acid sodium sulfate), oxalic acid, citric acid, phosphoric acid, and acetic acid. Combinations of these acids, for example, hydrochloric and sulfamic acid, formic and hydroxyacetic acid, sulfamic and hydroxyacetic acid may be used. When stainless steels are to be treated with compositions of this invention, these compositions may be used in combination with compositions for treating stainless steels disclosed in my U.S. Patents 2,793,190, 2,793,191, 2,806,300, 2,839,392 and 2,853,364.

The compositions of the present invention have a wide variety of uses. In addition to cleaning metal surfaces, coating weight determinations of phosphate coatings can be readily made by stripping the coating from a metal test panel. In addition, the compositions are effective in removing sludge which tends to build up in phosphatizing units.

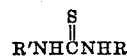
As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A composition for removing foreign matter from ferrous metal surfaces consisting essentially of an aqueous solution of from about 3% to about 15% of sulfuric acid, 0.75% to 18% of oxalic acid, from 0.025 gram per liter to 0.3 gram per liter of diorthotolylthiourea, and 0.01 to 3.5 grams per liter of sodium alkylphenyl sulfonate anionic surface active agent in which the alkylphenyl group contains an alkyl radical having a chain length of from 4 to 12 carbon atoms.

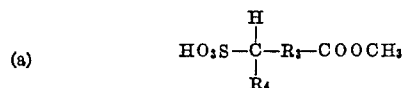
2. A process for removing foreign matter from a metal article which comprises cleaning said article by treating the surface thereof with an aqueous solution consisting essentially of from about 1% to about 30% by weight of a water soluble acid selected from the group consisting of sulfuric, hydrochloric, oxalic, sulfamic, formic, hydroxyacetic sodium bisulfate, phosphoric, citric, and acetic acid from about 0.025 gram per liter to saturation of a nitrogen containing compound selected from the group

consisting of thioureas and thioamides wherein said thioureas have the formula

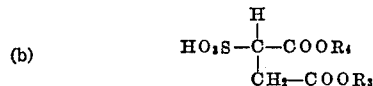


5 where R' and R are selected from the group consisting of alkyl radicals having a chain length of from 4 to 6 carbon atoms and phenyl and tolyl radicals, and said thioamides are selected from the group consisting of N-butylthiobutyramide, isobutylthioacetamide, N,N'-ethylene bithiobenzamide, N-phenylthiobenzamide, and N-isobutylthiobenzamide, and 0.01 to 3.5 grams per liter of an anionic surface active agent selected from the class consisting of alkali metal and amine alkyl sulfonates in which the alkyl group has a chain length of from 7 to 12 carbon atoms and alkali metal and amine alkylphenyl sulfonates in which the alkyl group has a chain length of from 4 to 12 carbon atoms, and sulfonated esters of mono- and dibasic carboxylic acids having the formula

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wherein R₃ and R₄ are alkyl radicals having a chain length of from 5 to 9 carbon atoms.

3. The process of claim 2 wherein said solution contains from 4% to 12% of sulfuric acid, 5% to 10% of oxalic acid, 0.1 to 3.0 grams per liter of said nitrogen-containing compound and from 0.01 to 1.0 gram per liter of said surface active agent.

4. A process for removing foreign matter from a ferrous metal article which comprises cleaning said article by treating the surface thereof with an aqueous solution consisting essentially of from 3% to 15% of sulfuric acid, 0.75% to 18% of oxalic acid, from 0.025 gram per liter to 0.3 gram per liter of diorthotolylthiourea, and 0.01 to 3.5 grams per liter of a sodium alkylphenyl sulfonate anionic surface active agent in which the alkylphenyl group contains an alkyl radical having a chain length of from 4 to 12 carbon atoms.

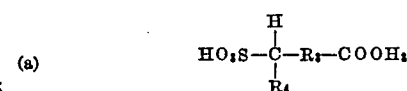
5. A process for removing foreign matter from a ferrous metal article which comprises cleaning said article by treating the surface thereof with an aqueous solution consisting essentially of 3% to 15% of sulfuric acid, 0.75% to 18% of oxalic acid, from 0.025 to 0.3 gram per liter of a nitrogen-containing compound selected from the group consisting of thioureas and thioamides wherein said thioureas have the formula

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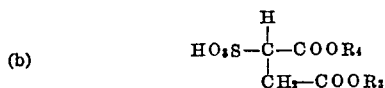
where R' and R are selected from the group consisting of alkyl radicals having a chain length of from 4 to 6 carbon atoms and phenyl and tolyl radicals, and said thioamides are selected from the group consisting of N-butylthiobutyramide, isobutylthioacetamide, N,N'-ethylene bithiobenzamide, N-phenylthiobenzamide, and N-isobutylthiobenzamide, and 0.01 to 3.5 grams per liter of an anionic surface active agent selected from the class consisting of alkali metal and amine alkyl sulfonates in which the alkyl group has a chain length of from 7 to 12 carbon atoms and alkali metal and amine alkylphenyl sulfonates in which the alkyl group has a chain length of from 4 to 12 carbon atoms, and sulfonated esters of mono- and dibasic carboxylic acids having the formula

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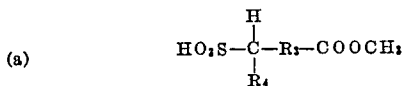


wherein R_3 and R_4 are alkyl radicals having a chain length of from 5 to 9 carbon atoms.

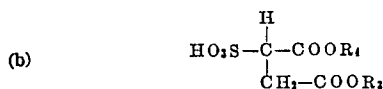
6. A composition for removing foreign matter from metal surfaces consisting essentially of an aqueous solution of from about 1% to about 30% by weight of a water soluble acid selected from the group consisting of sulfuric, hydrochloric, oxalic, sulfamic, formic, hydroxyacetic, sodium bisulfate, phosphoric, citric, and acetic acid from 0.025 to 0.3 gram per liter of a nitrogen-containing compound selected from the group consisting of thioureas and thioamides wherein said thioureas have the formula



where R' and R are selected from the group consisting of alkyl radicals having a chain length of from 4 to 6 carbon atoms and phenyl and tolyl radicals, and said thioamides are selected from the group consisting of N-butylthiobutyramide, isobutylthioacetamide, N,N'-ethylene bithiobenzamide, N-phenylthiobenzamide, and N-isobutylthiobenzamide, and 0.01 to 3.5 grams per liter of an anionic surface active agent selected from the class consisting of alkali metal and amine alkyl sulfonates in which the alkyl group has a chain length of from 7 to 12 carbon atoms and alkali metal and amine alkylphenyl sulfonates in which the alkyl group has a chain length of from 4 to 12 carbon atoms, and sulfonated esters of mono- and di-basic carboxylic acids having the formula



16



wherein R_3 and R_4 are alkyl radicals having a chain length of from 5 to 9 carbon atoms.

7. The composition of claim 6 wherein said solution contains from 4% to 12% of sulfuric acid, 5% to 10% of oxalic acid, 0.1 to 0.3 gram per liter of said nitrogen containing compound and from 0.01 to 1.0 gram per liter of said surface active agent.

8. The composition of claim 6 wherein said nitrogen-containing compound is diorthotolylthiourea.

9. The composition of claim 8 wherein said anionic surface active agent is dodecylbenzene sulfonate.

References Cited

UNITED STATES PATENTS

2,160,035	10/1935	Downing et al.	252—149
3,216,857	11/1965	Duvall	252—149
3,226,180	12/1965	Irwin	252—149

OTHER REFERENCES

Schwartz et al.—Surface Active Agents—Vol I, Interscience Publ. Page 100.

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U.S. Cl. X.R.

156—18; 134—3, 46

Disclaimer

3,481,882.—*Michael A. Streicher*, Webster Farms, Del. CLEANING COMPOSITION AND METHOD OF CLEANING ARTICLES THEREWITH. Patent dated Dec. 2, 1969. Disclaimer filed Nov. 24, 1972, by the assignee, *E. I. du Pont de Nemours and Company*.

Hereby enters this disclaimer to claims 2, 6, 8 and 9 of said patent.

[*Official Gazette March 13, 1973.*]