COMPOSITION AND METHOD FOR REMOVING COPPER CONTAINING IRON OXIDE SCALES FROM FERROUS METALS


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3,730,901

ABSTRACT OF THE DISCLOSURE

A method of and composition for removing copper and iron oxide containing incrustations from a ferrous metal surface so as to prevent or at least impede the formation of a curdy adhesive precipitate and utilize low ratios of copper complexor-to-copper.

A surface sought to be cleaned is contacted with an aqueous acid solution comprising a composite copper complexor composed of (i) hexahydropyrimidin-2-thione present as a first copper complexor in a concentration of from about 80% to about 20% by weight of the mixed complexor, and (ii) thiourea present as a second copper complexor in a concentration of from about 20% to about 80% by weight of the composite complexor. The composite copper complexor is present in solution in a weight ratio of at least 4:1 relative to the copper sought to be removed. The solution also includes an acid, selected from the group consisting of hydrochloric, sulfuric, sulfamic and phosphoric acids, and present in a concentration of from about 3% to about 30% by weight.

RELATED APPLICATIONS

This application is a continuation-in-part of parent application Ser. No. 56,987, filed July 6, 1970 now abandoned, and incorporates the disclosure of this parent application herein by reference. This application is also a continuation-in-part of application Ser. No. 138,410, filed Apr. 29, 1971 and now abandoned.

This present application also comprises a division of a "concurrent" application, Ser. No. 248,136, filed Apr. 27, 1972 entitled "Composition and Method for Removing Copper Containing Scales from Metals," designating John A. Knox, John A. Smith and Roy F. Stout as co-inventors, and assigned to the assignee of the present application.

This "concurrent" application discloses and claims, inter alia, a method and composition wherein copper containing scale is removed, with relatively high efficiency, from ferrous metal surfaces with an aqueous solution comprising the above-described mixture of compounds.

BACKGROUND AND SUMMARY OF INVENTION

General background

This invention relates to compositions for complexing copper ions. This invention also relates to compositions and methods for removing copper and copper compounds from a metal surface. It further relates to compositions and methods for removing copper, copper compounds, and iron oxide deposits from metal surfaces. This invention still further relates to the simultaneous removal of iron oxide scales and copper containing deposits from ferrous metal surfaces, such as those encountered in steam boilers.

In the operation of certain types of equipment, deposits containing copper, its oxides, and iron oxide frequently accumulate on the surface of the equipment. Where these deposits interfere with the efficient operation of the equipment they are removed. In recent years, it has been preferred to remove the deposits chemically; that is, chemically which dissolve the deposits are utilized.

Some solvents utilized to dissolve the deposits include aqueous solutions of certain acids. Thus when aqueous solutions of many acids are brought into contact with ferrous metal surfaces on which there is deposited copper metal and iron oxide, the iron oxide is ordinarily dissolved but the copper deposit is frequently not removed from the metal surface. Where the deposit contains an oxide of copper, it is ordinarily dissolved by the acid, but metallic copper will plate, i.e., redeposit, from the acidic solution on the ferrous metal surface. Thus the acid alone does not completely remove the offensive deposit.

Prior publications such as United States Martin et al., Patent 2,959,555 disclose that boiler cleaning formulations known at least as early as 1945 and comprising acidic solutions of thiourea may be used to simultaneously remove iron oxide, copper, and copper oxide from boilers.

Such solutions would be comprised of a first solvent component operable to dissolve, i.e., complex, the deposit, and a second component capable of preventing dissolved copper, i.e., copper ions, from depositing on a ferrous metal surface in contact with the removal solution. This second component has been referred to in the art, and will be referred to herein, as a "copper complexor."

Boiler cleaning compositions containing hydrochloric acid and thiourea which will perform this concurrent deposite dissolving and copper complexing function were disclosed in 1948 in United States Cardwell et al., Pat. 2,485,529 and in 1948 in United States Robinson Pat. 2,450,861. For example, solutions containing hydrochloric acid and thiourea in the amounts designated in claim 1 of Cardwell et al. (i.e. one percent thiourea in a five to twenty-five percent hydrochloric acid solution) and designated in lines 66-72 of column 4 of Robinson (i.e. one percent thiourea in a five to twenty-five percent hydrochloric acid solution) perform the boiler cleaning operation, with copper removal, disclosed by Martin et al.

Solution chemistry

When it is desired to remove metallic copper from a ferrous metal surface by a chemical solution, the solution, in addition to having copper-complexing ability, should possess the capability to convert the copper metal to the ionic form. This conversion capability is referred to herein as "oxidation." The oxidation capability is inherent in the acidic solvent component of the solution and may be enhanced through the introduction of an oxidizing substance which may be exteriorly added, such as free oxygen, or which may be produced by the solution reaction with a portion of the deposit itself, e.g., ferric ions formed from the ferric oxide in the scale.

Precipitate characteristic problems

In connection with the removal of the deposits, certain known copper complexors have been utilized individually with acidic solutions to facilitate the one-step removal of the copper and iron oxide from ferrous metal surfaces. However, whenever the copper complexor-copper weight ratio is low, many of the known copper complexors form an undesirable curdy, adhesive precipitate which may ultimately seriously damage the equipment sought to be cleaned. Thus, although some of the known copper complexors may be limitedly effective in maintaining copper in solution, they can allow insoluble copper complexes to be redeposited upon the equipment surface, before the cleaning operation is finished when excessive quantities of copper are present. Such redeposition is generally undesirable in industrial cleaning and can cause heat trans-
fer irregularities such as “hot spots” in industrial boilers. Presently used copper complexors require relatively high weight ratios of copper complexor-to-copper in order to satisfactorily remove copper incrustations without forming the above-mentioned undesirable precipitate. Compositions and methods have thus been sought which would permit the use of lower weights of copper complexor per unit weight of copper to be removed without the occurrence of replating and without the formation of the undesirable precipitate. Thiourea, 1,3-diethyl thiourea, monomethyl thiourea, and monoethyl thiourea are known to possess copper complexing ability; however, these complexors tend to form the undesirable curdy, adhesive precipitates when an insufficient concentration of copper complexor is present relative to the weight of the copper to be removed. Other known copper complexors are hexahydropyrimidin-2-thione, N-(2-hydroxyethyl)-ethylene thiourea, diethanol thiourea, and 4-methylimidazolidin-2-thione. Although this latter group of copper complexors avoids the problems of replating and the formation of an undesirable precipitate, they require the use of relatively high copper complexor-to-copper weight ratios. These and other problems are solved or at least substantially alleviated by the present invention which provides a composition and method for complexing copper ions.

**SUMMARY OF INVENTION**

**Concept of present application**

We have discovered a composition consisting essentially of a mixture of at least two compounds, which composition acts to complex copper ions to a degree not to be expected nor predicted from the complexing ability, when acting alone, of the individual compounds utilized in the mixture.

In another aspect we have discovered a high efficiency cleaning solution for the simultaneous removal of iron and copper deposits from metal surfaces comprising a solvent for dissolving the deposits and a composite copper complexor for preventing dissolved copper from forming new deposits on the metal surface. In still another aspect of this invention, there is provided a high efficiency method for the simultaneous removal of copper and iron deposits from a ferrous metal surface.

The cleaning solution of this invention effectively removes iron and copper deposits from ferrous metal surfaces without forming a curdy, adhesive precipitate, and without plating of dissolved copper from the cleaning solution on the metal surface. Furthermore, the copper complexing capability of the cleaning solution is surprisingly more efficient than heretofore known solutions in that the required weight of composite copper complexor per unit weight of copper removed is unexpec-

**Broader concept of concurrent application**

More broadly speaking, and as is treated in the aforementioned concurrent application, the copper complexor is a composition which consists essentially of mixtures of at least two compounds represented by the general formulae:

\[
R_1-CN-(CN)R_2
\]

and

\[
R_1-CN-(CN)R_2
\]

In Formula 1 above, \( R_1 \), \( R_2 \), \( R_3 \), \( R_4 \), and \( R_5 \) are hydrogen, straight or branched chain alkyl radicals having in the range of 1 to 3 carbon atoms, alkenyl radicals having in the range of 2 to 3 carbon atoms or mixtures thereof. In Formula 2 above, \( R_6 \) is a methylene group, i.e. a group, having 2 to 4 and preferably 2 to 3 carbon atoms,
i.e. \( m \) is an integer having a value in the range of 2 to 4, preferably 2 to 3, or a

\[
\text{C}_n\text{H}_m
\]

group wherein \( n \) is an integer having a value in the range of 0 to 3 and preferably 1 to 2, or a

\[
\text{C}_n\text{H}_m\text{C}=	ext{O}
\]

group; and \( R_1 \) and \( R_2 \) are hydrogen, a \(-\text{CH}_2\text{CH}_2\text{OH}\) group or mixtures thereof.

In one preferred broad embodiment, at least one of the \( R_1, R_2, R_3 \) and \( R_4 \) groups in the above Formula 1, and at least one of the \( R_1 \) and \( R_2 \) groups in the above Formula 2 are hydrogen.

In another preferred broad embodiment, each of the \( R_1 \) and \( R_3 \) groups in Formula 1, and each of the \( R_1 \) and \( R_2 \) groups in Formula 2 is hydrogen.

Compounds believed to be useful in the practice of the broad invention which are within the scope of Formula 1 above include but are not limited to:

- thiourea
- monomethyl thiourea
- 1,3-dimethyl thiourea
- monoethyl thiourea
- 1,3-diethyl thiourea
- triethyl thiourea
- mono-n-propyl thiourea
- 1,3-di-n-propyl thiourea

From the above list of compounds, those which are currently preferred for use herein are:

- thiourea
- monomethyl thiourea
- 1,3-dimethyl thiourea
- monoethyl thiourea
- 1,3-diethyl thiourea

Compounds believed to be useful herein which are within the scope of Formula 2 above include but are not limited to:

- ethylene thiourea
- N-(2-hydroxyethyl) ethylene thiourea
- hexahydropyrimidine-2-thione
- 1,3-di (2 hydroxyethyl) -hexahydropyrimidine-2-thione
- tetramethylene thiourea
- 1-(2-hydroxyethyl) -tetramethylene thiourea
- ethyldiene thiourea
- 1-(2-hydroxyethyl) -ethyldiene thiourea
- 4-methylimidazolidine-2-thione
- 1-(2-hydroxyethyl) -5-methylimidazolidine-2-thione
- 4-methylhexahydropyrimidine-2-thione
- 1,3-di (2 hydroxyethyl) -4-methylhexahydropyrimidine-2-thione
- 4-methyl (tetramethylene) thiourea
- 1,3-di (2-hydroxyethyl) -4-methyl (tetramethylene) thiourea.

From the above list of compounds, those which are currently preferred for use herein are:

- ethylene thiourea
- N-(2 hydroxyethyl) ethylene thiourea
- hexahydropyrimidine-2-thione
- 4-methylimidazolidine-2-thione.

In the mixture of compounds of the composition all of the compounds in any given mixture can be from Formula 1, all can be from Formula 2, or some can be from Formula 1 and some from Formula 2.

The quantity of at least one single compound (and preferably two) in the composite mixed copper complexor composition of the broad invention depicted by these formulas is not greater than about 90 parts by weight per 100 parts by weight of the mixture, and not less than about 10 parts by weight per 100 parts by weight of the mixture, the balance being one or more other copper complexors within the parameters of the above delineated formulas. It is contemplated that such a composite or mixture shall contain at least two copper complexor compounds within the parameters of Formula 1 and/or Formula 2 and that they shall be present within the above-mentioned proportions, but that other materials and compounds may be present in the solution without departing from the spirit or scope of the composition of this invention.

In the preferred embodiments of our broader invention the quantity of at least one compound in the mixture is not greater than about 80 parts by weight per 100 parts by weight of the mixture.

Accordingly, in the preferred embodiments of the broader invention, two-component mixtures have extreme composition limits for a single component of about 80 to about 20 parts by weight per 100 parts by weight of the mixture. Thus, for example, in the mixture thiourea plus hexahydropyrimidine-2-thione, thiourea is preferably present in the range of about 80 to 20 parts by weight per 100 parts by weight of the mixture and hexahydropyrimidine-2-thione is preferably present in the range of about 20 to 80 parts by weight per 100 parts by weight of the mixture.

Further, in the preferred embodiments of the broader invention, compositions having more than two copper complexor compounds in the mixture have extreme composition limits for at least one component (and preferably two) in the range of not greater than about 80 parts by weight and not less than about 10 parts by weight per 100 parts by weight of mixture. Thus, by way of example, a three-component mixture can have 80 parts by weight of one compound and 10 parts by weight of each of two other compounds; and, in another example, a ten-component mixture can have 10 parts by weight for each compound in the mixture.

It has been previously stated that the above-described mixed copper complexor composition of this broader invention is useful to complex copper ions. Accordingly, copper dissolved in any solution is complexed by merely adding to the copper ion-containing solution the composition of this invention. In this regard there is no known maximum quantity of copper complexor required to complex a given amount of copper except that as dictated by economics. However, it is considered that a reasonable quantity of complexor of this invention is in the range of about 2 to 50 parts by weight per one part by weight of copper to be removed.

It is believed that the composition of this broader invention can complex copper dissolved in other than acidic solutions; however, it is preferred that the pH of the solution is, or is adjusted to about 5 or less.

As previously stated, this invention also provides an aqueous cleaning solution for the simultaneous removal of iron and copper deposits from metal, particularly ferrous metal, surfaces. The cleaning solution of this invention is comprised of a solvent for the iron and copper deposits, the mixed copper complexor composition described above, and water; the solvent is present in the cleaning solution in the range of about 0.5 to 50 percent by weight of the solution and the copper complexor of this invention is present in the cleaning solution in the range of about 0.1 to 5, preferably 0.2 to 4, and still more preferably 0.4 to 3 percent by weight of the solution with
the remaining weight of the solution being substantially water.

The copper complexor utilized in the cleaning solution of this broader invention is the mixed composition described hereinabove and reference is accordingly made to that description.

The solvent useful in the cleaning solution is any acid or acid material capable of dissolving iron and copper deposits. Suitable acids include hydrochloric acid, hydrofluoric acid, sulfuric acid, sulfamic acid, phosphoric acid and mixtures thereof, wherein hydrochloric acid is the most preferred acid for use in the present invention. Other useful acids are citric acid, acetic acid, gluconic acid, formic acid, and other organic acids and mixtures thereof. The acid is preferably used in concentrations in the range of about 0.5% to about 30% by weight of the solution. Concentrations of less than about 0.5% tend to be ineffective in dissolving the copper-containing iron oxides, and concentrations above about 30% often demonstrate excessive corrosion on the ferrous surface sought to be cleaned.

Acidic materials, useful in the practice of the broader invention, in addition to the above-named acids also include acid salts such as sodium bisulfate, sodium bifluoride, mono-sodium citrate, potassium bisulfate, and the like.

The preferred acids and quantities in percent by weight of cleaning solution are hydrochloric acid, 3 to 10%; sulfuric acid, 5 to 15%; sulfamic acid, 3 to 10%; and phosphoric acid, 10 to 25%.

Because in some instances there is a tendency to experience corrosiveness of the acid cleaning solution with respect to the ferrous metal surface, it is frequently necessary to use a corrosion inhibitor as an optional element of the composition of the present invention. Any commercially available corrosion inhibitor may be used which is suitable for the acid selected. Such inhibitors are ordinarily used in amounts in the range of 0.01 to 1.0 percent by volume of the cleaning solution.

It has been found that an auxiliary oxidant present in the aqueous acid solution greatly increases the rate at which the copper becomes available to the complexor. It is being that the auxiliary oxidant enhances the transformation of metallic copper to ionic copper. The oxidant may be the ferric ions which occur naturally in the iron inclusions on the ferrous metal surface sought to be cleaned, oxygen in the aqueous acid solution, or any other oxidant capable of changing the elemental copper to cuprous (or possibly cupric) ions.

Mode of practice of invention

It has been found that the components of the present invention do not interact chemically with each other prior to contacting the copper. However, when the complexor of this invention is used, a mixed complex is formed with copper which is different from the reaction product formed with copper when only one component is used. The mixed complex formed with copper and the complexor of this invention has been found, through X-ray crystallography, to have a different crystalline structure than the reaction product formed with copper when only one component is used.

The metal surface to be cleaned is contacted by the cleaning solution of this invention by any suitable method, e.g., soaking, pouring, spraying, circulating, and the like. The cleaning solution of this invention is particularly suitable for cleaning the inside of vessels of complex shapes where formation of a curdy, adhesive precipitate can present difficult removal problems. Normally, the area to be cleaned is contacted by filling the vessel with the cleaning solution of this invention. It is found that copper removal can be particularly enhanced by stirring or other suitable means of agitation during the contacting step.

During the contacting step, the temperature of the solution is typically maintained in the range of 50° F. to 175° F., and preferably 120° to 160° F., for a period of time sufficient to dissolve the deposits. This time is generally in the range of from about 2 to 12 hours, preferably about 4 to 8 hours. Where acids such as sulfuric acid are employed, operating temperatures beneath 150° F. may be desired to ensure that the complexors do not deteriorate.

In this connection, it has also been discovered that the corrosion rates of normally inhibited hydrochloric acid on ferrous metal surface are reduced when the preferred concentration of the composition of the present invention is used as compared with corrosion rates demonstrated by the acid when 100% hexahydroimiduridine-2-thione or 100% thiouria is used.

EXAMPLES

Presently preferred embodiment

The presently preferred embodiment of the invention entails the use of a composite copper complexor comprising hexahydroimiduridine-2-thione and thiouria in a solution of hydrochloric acid.

The surprising effect of using this composite copper complexor formulation is that it is synergistic, rather than additive, in its effect on the efficiency of copper removal in pounds of copper removed per pound of mixed complexor used. The mixed complexor also provides the feature of eliminating redeposition of copper during the complexing operation and eliminating the formation of an undesirable precipitate.

The “most preferred” concentration of the hexahydroimiduridine-2-thione is about 60% by weight of composite complexor, with thiouria comprising the remaining 40% by weight of the composite complexor. If less than 10% by weight of composite complexor or greater than 90% by weight of composite complexor of the hexahydroimiduridine-2-thione is present in the composition of the present invention, the significant synergistic effect on the efficiency of the composite complexor over the efficiency of its separate constituents is lost. A sharp decrease in the efficiency of the composite complexor occurs when the concentration of hexahydroimiduridine-2-thione is decreased from about 20% by weight of composite complexor to about 10% by weight of composite complexor. A similar sharp decrease in the efficiency of the composite complexor occurs when the concentration of hexahydroimiduridine-2-thione is increased from about 80% to about 90% by weight of composite complexor.

The thiouria may be present in a concentration of from about 10% to about 90% by weight of composite complexor, although the preferred range of concentration of thiouria is from about 20% to about 80% by weight of composite complexor, and the most preferred concentration is about 40% by weight of composite complexor. The significant synergistic effect of the composite complexor is lost if less than about 10% by weight of composite complexor, or greater than about 90% by weight of composite complexor, of thiouria is present in the mixture. The greatest improvement in the efficiency occurs when the concentration of thiouria is reduced from about 90% to about 80% by weight of composite complexor, or increased from about 10% to about 20% by weight of composite complexor.

The weight ratio of mixed copper complexor-to-copper should most preferably be at about 8:1. A complexor-to-copper weight ratio of 4:1 or greater can complex copper from copper-containing iron inclusions on a ferrous surface without floculent precipitation. Concentrations of mixed complexor lower than about four parts complexor to about one part copper can result in the formation of a flocculent (i.e. dispersible) easily-pumpable precipitate which is not curdy or adhesive, and is not considered harmful to most industrial equipment sought to be cleaned. There is no maximum amount of copper complexor which may be used to complex a given amount of copper except that maximum amount dictated by economics.
To avoid turbidity in the cleaning solution, the minimum mixed complexor concentration of about five parts of mixed complexor to about one part copper for the present invention is to be compared with a minimum concentration of about nine parts complexor to one part copper for thiourea. A complexor-to-copper ratio of thiourea less than about 9:1 will result in a curdy, adhesive precipitate which is generally thought of as being undesirable. The minimum concentration of hexahydropyrimidine-2-thione which may be used prior to the formation of a precipitate is about 8.5:1, although the precipitate formed by using insufficient amounts of hexahydropyrimidine-2-thione is a flocculent (i.e. dispersible), easily-pumpable precipitate which is not generally considered to be harmful.

The acid is normally used in an aqueous solution with suitable concentrations being in the range of from about 3% to about 30%. Concentrations of less than about 3% may at times tend to be less than desirably effective in dissolving the copper-containing iron oxides, and concentrations above about 30% may demonstrate excessive corrosion on the ferrous surface sought to be cleaned.

Because of the corrosiveness of the incrustation, removing acid solution with respect to the ferrous surface, it is frequently necessary to use an acid corrosion inhibitor as an optional element of the composition of the present invention. Any commercially available corrosion inhibitor may be used which is suitable for the acid selected.

The following examples are provided to further illustrate the presently preferred form of our invention, but are not to be construed to in any way limit the scope thereof. These examples are presented in the post set forth in parent application Ser. No. 56,987.

EXAMPLE I

Test procedure

Five tenths gram of each copper complexor composition described in Table I, below is weighed out and dissolved in 80 to 90 milliliters distilled water and titrated with a solution containing 0.15 gram of CuCl₂ per 25 milliliters concentrated HCl at 150° F. with constant stirring. The ratio of complexor-to-copper is noted at which a definite turbidity is observed. Table I, below, shows the "most preferred" copper complexor composition is 60% hexahydropyrimidine-2-thione and 40% thiourea at a complexor-to-copper ratio of 5:23:1.

TABLE I

<table>
<thead>
<tr>
<th>Complexor composition, percent</th>
<th>Copper, ppm</th>
<th>Complexor: copper, ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>100</td>
<td>5.95</td>
</tr>
<tr>
<td>Thiourea</td>
<td>100</td>
<td>8.95</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>8.95</td>
</tr>
</tbody>
</table>

EXAMPLE II

The following copper dissolution tests are each run in 100 ml. of 5% hydrochloric acid containing 0.2% by weight of a commercially available corrosion inhibitor at 150° F. for six hours. Each test sample contains 0.75 gram of powdered magnetite and 0.10 gram powdered copper metal. Varying weights of the aforesaid most preferred embodiment of the mixed complexor (0.60 gram, 0.80 gram, and 1.00 gram) are used in the tests. Table II, below, shows the present invention in the aforesaid "most preferred" embodiment has a greater copper complexing efficiency than either hexahydropyrimidine-2-thione or thiourea used alone.

TABLE II

<table>
<thead>
<tr>
<th>Complexor</th>
<th>Copper found, mg.</th>
<th>Percent dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present invention</td>
<td>101</td>
<td>90</td>
</tr>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>Thiourea</td>
<td>77</td>
<td>65</td>
</tr>
<tr>
<td>Present invention</td>
<td>101</td>
<td>90</td>
</tr>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>Thiourea</td>
<td>77</td>
<td>65</td>
</tr>
<tr>
<td>Present invention</td>
<td>101</td>
<td>90</td>
</tr>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>Thiourea</td>
<td>77</td>
<td>65</td>
</tr>
</tbody>
</table>

EXAMPLE III

Test procedure

Corrosion rate tests are run using preweighed coupons which are soaked for six hours at 150° F. in normally inhibited 5% hydrochloric acid solutions containing both 1% and 0.5% of the aforesaid "most preferred" embodiment of the mixed complexors of the present invention and of hexahydropyrimidine-2-thione and thiourea. Table III, below, shows that the corrosion rate in pounds per foot per day on the steel coupon is less when the present inventive composition is used than when either of its preferred ingredients are used alone.

TABLE III

<table>
<thead>
<tr>
<th>Complexor</th>
<th>Contraction, percent</th>
<th>Corrosion rate, lb./sq. ft./day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present invention</td>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>Thiourea</td>
<td>1</td>
<td>0.07</td>
</tr>
<tr>
<td>Present invention</td>
<td>0.5</td>
<td>0.009</td>
</tr>
<tr>
<td>Hexahydropyrimidine-2-thione</td>
<td>0.5</td>
<td>0.018</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.5</td>
<td>0.010</td>
</tr>
</tbody>
</table>

EXAMPLE IV

Test procedure

Tests are run to determine whether the present invention is a composite of two copper complexors or a compound resulting from a chemical reaction between hexahydropyrimidine-2-thione and thiourea. Cuprous chloride dissolved in concentrated hydrochloric acid is added to solutions containing hexahydropyrimidine-2-thiones, thiourea, and the present invention. When sufficient copper is added to the aforesaid "most preferred" embodiment of the present invention so that lower coordination complexes, precipitation occurs. Infrared spectra of the precipitated complexes are made. Observation of the infrared spectra indicates both hexahydropyrimidine-2-thione and thiourea characteristics as well as modification characteristics.
11 Observations

(A) A doublet at 3150 cm\(^{-1}\) and 3350 cm\(^{-1}\) is observed (characteristic of the primary NH\(_2\) stretching mode of thiourea).

(B) C-H stretch peaks at 2880 cm\(^{-1}\) and 2980 cm\(^{-1}\) are observed. Since thiourea has no C-H groups, it is believed the stretch peaks are due to the C-H groups in hexahydropyrimidine-2-thione.

(C) A broad absorption between 400 cm\(^{-1}\) and 650 cm\(^{-1}\) is observed and thought to be due to a strong NH deformation present in the primary amide group of thiourea. Hexahydropyrimidine-2-thione has no primary amide groups.

The aforesaid infrared spectrographic data, in conjunction with the synergistic action of the "mixed" complexor supports the conclusion that a unique, composite, complexing action occurs.

EXAMPLE V

Test procedure

Solutions containing 5\% inhibited hydrochloric acid and 0.52\% cuprous chloride plus 1.33\% magnetite are mixed with various concentrations of thiourea and hexahydropyrimidine-2-thione and with the mixed complexor of the present invention at various ratios of thiourea-totetrahydroxypyrimidine-2-thione. A steel coupon is added to each solution and the solutions are maintained at 150° F. for six hours in a constant temperature bath. At the end of the test period, the solutions and steel coupons are visually inspected to determine the presence of copper plating on the steel coupon and a precipitate in the solution. Table V, below, shows the aforesaid "most preferred" embodiment of the present invention provides an absence of copper plating and an absence of undesirable curdy, adhesive precipitate in complexor-to-copper ratios of about 4:1 and greater.

<table>
<thead>
<tr>
<th>Complexor concentration, weight percent</th>
<th>Thiourea</th>
<th>Hexahydropyrimidine-2-thione</th>
<th>Coupon condition</th>
<th>Solution condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>80</td>
<td>20 LP</td>
<td>VH</td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>80</td>
<td>20 LP</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>0.67</td>
<td>80</td>
<td>20 LP</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>0.73</td>
<td>80</td>
<td>20 LP</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>0.87</td>
<td>80</td>
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<td>M</td>
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</tr>
<tr>
<td>0.93</td>
<td>80</td>
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<td>M</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>80</td>
<td>20 VLP</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>80</td>
<td>20 N</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>2.20</td>
<td>80</td>
<td>20 N</td>
<td>S</td>
<td></td>
</tr>
</tbody>
</table>

1 By percent weight of solution.

Explanation of symbols—N=No copper plated on coupon; MP= Moderate copper plate; LP=Light copper plate; VLP=Very light copper plate; G=Solution gelled; (VL=Large amount of precipitate greater than 60\% of solution volume); H=90-95\% solution volume as precipitate; M=35-50\% solution volume as precipitate; S=Solution turbid; T=Small (less than 5\%) amount of precipitate at bottom of container.

Broad invention

At this juncture, and in order to delineate certain "broader" aspects of the invention which are treated in the aforesaid concurrent application, reference will now be made to results of a broad gauge test program which has been conducted.

In this connection, it will be recognized that the foregoing data is presented in a somewhat different format than that heretofore discussed, and may in certain instances be subject to the normal variations and refinements involved in reorganizing and refining data.

In all of the examples which follow, the individual complexors utilized are identified by the capital letters A through I, inclusive. The following list sets out the complexor and the letter by which it is identified:

A—Thiourea
B—Monomethyl thiourea
C—Monoethyl thiourea
D—Hexahydropyrimidine-2-thione
E—N-(2-hydroxyethyl)-ethylene thiourea
F—Ethylene thiourea
G—4-methylimidazolidine-2-thione
H—1,3-dimethyl thiourea
I—1,3-dimethyl thiourea

EXAMPLE VI

One-half gram of copper complexor is dissolved in about 85 milliliters of distilled water. The resulting copper complexor solution is titrated with an acid solution containing cuprous chloride.

The acid titrating solution is prepared by dissolving in concentrated reagent grade hydrochloric acid (37.5 parts by weight HCl per 62.5 parts by weight water) about 0.005 gram cuprous chloride per milliliter of the concentrated acid.

The titration is conducted in a 200 milliliter Berzelius tall form beaker at 150° F. With stirring to a turbid endpoint which is reached when a thermistor temperature sensor placed in approximately the middle of the beaker within the titrated solution can no longer be seen.

Results of the titration are set out in Table IV below. In Table VI the total weight of complexor utilized, whether singly or in admixture, is shown to be constant at 0.5 gram for each run. In those runs where more than
one complexer is indicated, then the individual complexers are present in each mixture in equal weights.

13 The above general rule, however, does not hold with respect to runs 13, 15, 16, 17, 37, 38, 39 and 40. Approximately, in run 12 there are 0.4 gram ((0.8)/(0.5)=0.4), and 0.1 gram D ((0.2)/(0.5)=0.1); in run 13 there are approximately 1.5 hours in order to also form iron oxide on the inside surface of the pipe. Accordingly, the inside of each pipe is encrusted with iron oxide and copper. The weight of copper plated on each pipe and the complexor-to-copper weight ratio for each solution is set out in Table VII-B below.

### Table VII-A

<table>
<thead>
<tr>
<th>Number</th>
<th>Weight, HCl, HNO₃, H₂O</th>
<th>Complexer, by wt.</th>
<th>HCl, HNO₃, H₂O, by wt.</th>
<th>percent, by wt.</th>
<th>Percent HCl, HNO₃, H₂O, by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>247.9</td>
<td>2.4</td>
<td>12 223.5</td>
<td>9,968</td>
<td>4,841</td>
</tr>
<tr>
<td>2</td>
<td>248.2</td>
<td>1.44</td>
<td>12 233.5</td>
<td>9,983</td>
<td>4,86</td>
</tr>
<tr>
<td>3</td>
<td>248.2</td>
<td>1.68</td>
<td>12 233.5</td>
<td>9,983</td>
<td>4,86</td>
</tr>
</tbody>
</table>

1 Each solution contains 0.46 ml. of acid corrosion inhibitor which is the reaction product of a malic acid with an aldehyde and a ketone plus an acetysalicylic acid plus a polyethyleneimine polymer.

2 See Table VII-C for the specific complexers utilized in each run.

### Table VII-B

<table>
<thead>
<tr>
<th>Copper plate</th>
<th>Copper ratio</th>
<th>Weight, wt.</th>
<th>Complexer, by wt.</th>
<th>HCl, HNO₃, H₂O, by wt.</th>
<th>percent, by wt.</th>
<th>Percent HCl, HNO₃, H₂O, by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>101c</td>
<td>95.2</td>
<td>95.2</td>
<td>93.2</td>
<td>95.2</td>
</tr>
<tr>
<td>2</td>
<td>0.24</td>
<td>61</td>
<td>95.2</td>
<td>95.2</td>
<td>93.2</td>
<td>95.2</td>
</tr>
<tr>
<td>3</td>
<td>0.24</td>
<td>71</td>
<td>95.2</td>
<td>95.2</td>
<td>93.2</td>
<td>95.2</td>
</tr>
</tbody>
</table>

### Table VII-C

<table>
<thead>
<tr>
<th>Complexer</th>
<th>CuCl₂-HCl solution, ml</th>
<th>H₂O, HNO₃, H₂O, grav.</th>
<th>Complexer, by wt.</th>
<th>Copper ratio</th>
<th>Weight, wt.</th>
<th>Wt. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.2 0.0547 6.310 95.82</td>
<td>100 350</td>
<td>0.498 16.17 93.35</td>
<td>5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-B</td>
<td>17.7 0.0692 7.04 97.75</td>
<td>105 894</td>
<td>0.472 7.22 93.31</td>
<td>7.55 12 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-+H-0.20D</td>
<td>17.7 0.0681 7.04 97.75</td>
<td>105 894</td>
<td>0.472 7.22 93.31</td>
<td>7.55 12 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-0.44A+D</td>
<td>17.7 0.0681 7.04 97.75</td>
<td>105 894</td>
<td>0.472 7.22 93.31</td>
<td>7.55 12 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-0.4+D</td>
<td>17.7 0.0681 7.04 97.75</td>
<td>105 894</td>
<td>0.472 7.22 93.31</td>
<td>7.55 12 9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table VII above clearly shows that the weight of mixed complexer actually required to complex copper without significant precipitate formation is unexpectedly lower than the weight which would be predicted from the complexing ability of each individual complexer in the composite when acting alone.

### EXAMPLE VII

Cleaning solutions consisting of various copper complexers, hydrochloric acid, an acid corrosion inhibitor, and water are prepared by mixing the above components together in the amounts set out in Table VII--A below.

Each cleaning solution is then placed in a 2½-inch nominal diameter by 4-inch long mild steel nipple (ASTM A53) having a rubber stopper in one end and being open on the other end. Each pipe is previously plated on the inside surface thereof with copper, and treated in a steam atmosphere at 900°F. to 1000°F. for 5,780,901.

The cleaning solution is maintained in each nipple at 150°F. with gentle stirring for 5 hours after which time the solution is analyzed for dissolved copper.

The actual quantity of copper recovered from the nipples by the cleaning solution is reported in Table VII--C below. In terms of the weight percent of copper originally plated on the nipple. Also set out in Table VII-C, for purposes of comparison, is the weight percent of copper which would be predicted to be removed based on the removal ability of solution containing only one complexer acting alone.

In Tables VII--A and VII--C the total weight of complexer utilized, whether singly or in admixture, is shown to be constant for each solution, i.e., solution 1, 2, 4, 4 grams; solution 2, 1.44 grams; solution 3, 1.68 grams. In those rows where more than one complexer is indicated, the individual complexers are present in each mixture in equal weights.
The above general rule, however, does not hold with respect to runs 11, 34, 35, 36, and 37. Accordingly, in run 11, solution 1, there are 0.96 gram Complexor A and 1.44 gram of Complexor D; and in solution 2 there are 0.576 gram of Complexor A and 0.864 gram of Complexor D. In runs 34, 35, 36, and 37, Complexors A and D are present in constant weights in solution 1 at 0.648 gram and 0.96 gram respectively. Complexors B, C, F, and G are present in equal weights in runs 34, 35, 36, and 37 of 0.792 gram in solutions 1 and 0.4752 gram in solutions 2.

### TABLE VII-C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Complexor composition</th>
<th>Solution 1, actual</th>
<th>Solution 2, Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>G</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>9</td>
<td>I</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>A+B</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>A+E + B</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>A+C</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>13</td>
<td>A+D</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>14</td>
<td>A+F</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>A+G</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>16</td>
<td>A+H</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>17</td>
<td>A+B + C</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>A+B + E</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>19</td>
<td>A+B + F</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>20</td>
<td>A+B + G</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>21</td>
<td>A+B + H</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>22</td>
<td>A+C + D</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>23</td>
<td>A+C + E</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>24</td>
<td>A+C + F</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>25</td>
<td>A+C + G</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>26</td>
<td>A+C + H</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>27</td>
<td>A+D + E</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>28</td>
<td>A+D + F</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>29</td>
<td>A+D + G</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>30</td>
<td>A+D + H</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>31</td>
<td>A+E + F</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>32</td>
<td>A+E + G</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>33</td>
<td>A+E + H</td>
<td>53</td>
<td>53</td>
</tr>
</tbody>
</table>

Table VII-C above clearly shows that the cleaning solutions containing a mixture of complexors generally remove surprisingly more plated copper than would be predicted from the removal ability of the individual complexors in the mixture when acting alone.

### EXAMPLE VIII

Cleaning solutions consisting of various solvents, corrosion inhibitors compatible with the particular solvent, water, and a mixed copper complexer consisting of 40 parts by weight thiourea per 100 parts by weight of the mixture and 60 parts by weight of hexahydropyrimidine-2-thione per 100 parts by weight of the mixture, are prepared by mixing the above components together in the concentrations set out in Table VIII below.

Each cleaning solution is then placed in a 2¼ inch nominal diameter by 4-inch long mild steel pipe nipple (ASTM A-53) having a rubber stopper in one end and being open on the other end. Each pipe is previously plated on the inside surface thereof with 0.12 gram of copper and thereafter treated in a steam atmosphere at 900°F. to 1000°F. for approximately 1.5 hours in order to also form iron oxide on the inside surface of the pipe. Accordingly, the inside of each pipe is incrust with iron oxide and copper. The weight of mixed complexor utilized in each cleaning solution is adjusted such that the complexor-to-copper weight ratio for each solution is 10 parts by weight complexor per 1 part by weight copper.

Runs 1 through 13 inclusive each utilize 241.2 grams of cleaning solution and runs 14 and 15 each utilize 251.25 grams of cleaning solution.

Each cleaning solution contains 0.1% by volume of the total volume of the solution of a compatible copper inhibitor.

The cleaning solution is maintained in each nipple at the temperature indicated in Table VIII with gentle stirring for 5 hours after which time the solution is analyzed for dissolved copper.

The actual quantity of copper removed from the nipple by the cleaning solution is reported in Table VIII below in terms of the weight percent copper originally plated on the nipple.

In Example VIII which follows, the individual solvents utilized are identified by capital letters. The following list sets out the solvent and the letter by which it is identified:

- J — Sodium bisulfate
- K — Ammonium bisulfate
- L — Citric acid
- M — 0.09 part by weight ammonia (NH3)+1 part by weight of citric acid
- N — Sulfamic acid
- O — 89 parts by weight of sulfamic acid+6 parts by weight of citric acid
- P — 3 parts by weight of sodium bisulfate+1 part by weight of citric acid
- Q — 3 parts by weight of ammonium bisulfate+1 part by weight of citric acid
- R — 94 parts by weight of sodium bisulfate+1 part by weight of citric acid
- S — 94 parts by weight of ammonium bisulfate+1 part by weight of citric acid
- T — Sulfuric acid, H2SO4
- V — Phosphoric acid, H3PO4
- W — Hydrofluoric acid, HF
- Z — 2 parts by weight hydroxyacetic acid+1 part by weight of formic acid

### TABLE VIII

<table>
<thead>
<tr>
<th>Solvent number</th>
<th>Solvent</th>
<th>Compositions</th>
<th>Quantity, gm.</th>
<th>Percent Copper removed, wt.</th>
<th>Percent H2O, by wt.</th>
<th>Percent HCl, by wt.</th>
<th>Wt. ratio of complexor to copper</th>
<th>Treating temperature, °F.</th>
<th>Copper removed, wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>E</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>11.4</td>
<td>0.49</td>
<td>4.73</td>
<td>94.78</td>
<td>10.1</td>
<td>175</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>
From Table VIII it is clearly seen that the mixed complexor of this invention is useful to remove copper in the presence of a number of solvents.

### SUMMARY OF ADVANTAGES

An advantage of the copper complexor of the present invention is that a lower ratio of mixed complexor-to-copper can be used without the formation of any precipitate than was previously possible.

An additional advantage of the mixed copper complexor of the present invention is that it provides copper removal at surprisingly lower ratios of complexor used to copper removed than was previously available.

Still another advantage of the mixed copper complexor of the present invention is that when insufficient amounts of the mixed complexor are used, the precipitate formed is dispersed and easily pumpable, in contrast with the curdy, adhesive precipitate formed when insufficient amounts of some individual thiourea derivatives are used.

Also, an advantage of the mixed copper complexor of the present invention is that, in its preferred embodiment, the complexor will not replate copper when used in a copper complexor-to-copper ratio of at least about 4:1.

An additional advantage of the mixed copper complexor of the present invention is that it provides reduced acid corrosion of the ferrous surface sought to be treated.

These aforesaid advantages are uniquely important and significant in connection will the cleaning of industrial steam boilers.

The surprising effect of mixing the copper complexors in the aqueous acid solution is that it is synergistic rather than additive in its effect on the efficiency of copper removal per pounds of mixed complexor used and, as noted, the mixed complexor also provides the features of substantially eliminating redeposition of copper during the complexing operation and substantially eliminating the formation of an undesirable precipitate.

With the respect to the presently preferred embodiment, it is, of course, true that both hexahydropyrimidine-2-thione and thiourea have heretofore been individually known as complexors for copper which are useful in acid descaling solutions. The use of the former for this purpose is disclosed in United States Frost et al. Pat. 3,547,697 and the use of the latter for this purpose is disclosed in the earlier noted United States Martin et al. Pat. 2,959,555. By the same token, the foregoing examples and tables clearly and unambiguously show that these two known copper complexors, in combination, exhibit a quite pronounced and unexpected synergism.

For instance, data in Table I show that the mixed copper complexor of the present composition containing, for instance, 80% thiourea and 20% hexahydropyrimidine-2-thione is capable of holding an amount of copper in solution which corresponds to a complexor: copper ratio of 5.9:1, a mixed copper complexor containing 40% thiourea and 60% hexahydropyrimidine-2-thione is capable of holding copper in solution in an amount corresponding to a complexor: copper ratio of 5.2:1, and a mixed complexor composition containing 20% thiourea and 80% hexahydropyrimidine-2-thione is capable of holding copper in solution in an amount corresponding to a complexor: copper ratio of 6.4:1. By contrast, when thiourea is used as the sole copper complexor in the solution, the amount of copper which it holds in solution corresponds to a complexor: copper ratio of 8.95, i.e. the amount of complexor required to hold a given amount of copper in solution is from about 38.5 to 71% greater when thiourea is used as the sole complexor than when any of the mixed complexors listed in Table I are used. Similarly, it can be shown that when hexahydropyrimidine-2-thione is used as a sole copper complexor, the amount of this copper complexor which is required to hold a given quantity of copper in solution is from 34% to 65% greater than any of the mixed copper complexor compositions listed in Table I. In fact, the Table I data, when extrapolated, will show that when a mixed copper complexor is used containing only 10% thiourea and 90% hexahydropyrimidine-2-thione or 10% thiourea and 10% hexahydropyrimidine-2-thione, about 7.5 parts of such a mixed complex is capable of holding as much copper in solution as 8.9 parts of a composition wherein thiourea is a sole complexor or as 8.64 parts of a composition wherein hexahydropyrimidine-2-thione is the sole complexor. In other words, as such an extrapolation will show, even when a mixed complexor is used containing only 10% of thiourea and 90% hexahydropyrimidine-2-thione (and vice versa), it is more efficient than either of its components individually in that about 23.5% more hexahydropyrimidine-2-thione or about 28.5% more thiourea is required to hold the same amount of copper in solution than when a mixed complexor containing 10% of one and 90% of the other copper complexor is used.

The data in Example II further substantiates the various unexpected differences which make the mixed complexor so greatly superior to either of its known components individually. In this connection it is significant to observe with reference to the data shown in Table II that the superiority of the claimed mixed complexor over its individual components is particularly pronounced at the lower copper-to-complexor ratios.

The important practical significance of this set of data is that even if a relatively high proportion of complexor is used in the descaling solution relative to the total amount of copper which is estimated to be in the scale to be removed, normally such copper is not evenly distributed throughout the system but tends to be concentrated in certain areas. Consequently, even though the overall complexor: copper ratio is relatively high and theoretically sufficient to hold all the copper in solution, in this area where the copper deposits are concentrated the local ratio of complexor-to-copper will be significantly lower. In the case of a relatively inefficient complexor such as thiourea alone this then increases the risk that some of the dissolved copper will be redeposited as insoluble copper complexes on the cleaned steam generator surface and ultimately lead to failure due to resulting hot spots during the course of steam generation.

Furthermore, as is indicated by the data in Example IV, when the mixed copper complexor of the presently preferred embodiment sequesters dissolved copper ions, it forms a mixed copper complex which is essentially different from the simple type of copper complex which is formed when either thiourea alone or hexahydropyrpimidine-2-thione alone is used as the copper complexor. In other words, the mixed copper complexor of this invention operates by a chemical mechanism which is distinct from the simple reactions of either of its components and produces an important improvement in complexor efficiency.

To sum up, the present invention departs from the teachings of patents such as Frost et al., or Martin et al. because

(a) the claimed invention involves the use of different means (a composite complexor comprising interacting hexahydropyrimidine-2-thione and thiourea, as opposed to the prior use of either of these two complexors individually),

(b) the invention operates by a different mechanism by forming copper complexes which are different from and more soluble than the complexes formed by either of these two complexors individually, and

(c) the invention leads to a significantly different result in that substantially lower concentrations of the composite copper complexor are required than in the case of either its components, the difference being attributable to an unexpected synergism between the two components.

Thus, in light of this phenomena and the foregoing discussion, it will be clear that, while complexing copper in acid solution, the "mixed" complexor or "mixture" of
this invention does not entail a mere simple additive formulation. Rather, while acting in solution to complex copper, this “mixed” complexor functions as a uniquely composite, somehow interacting formulation, which yields results not attainable by any individual complexor used as a raw solution ingredient.

Having described our invention that which is claimed is:

1. An acid cleaning solution for the simultaneous removal of copper and iron deposits from a ferrous metal surface while precluding redeposition of copper and the formation of a curdy adhesive precipitate at low complexor-to-copper ratios comprising:

(a) an aqueous solution selected from the group consisting of hydrochloric acid, sulfuric acid, sulfamic acid and phosphoric acid, said acid solution having an acid concentration in the range of from about 3% to about 30% by weight, and
(b) hexahydropriimidine-2-thione and thiourea as a mixed copper complexor, said hexahydropriimidine-2-thione being present in a concentration of from about 20% to about 80% by weight of said mixed copper complexor and said thiourea being present in a concentration of from about 80% to about 20% by weight of said mixed copper complexor, and said mixed copper complexor being present in said acid solution in a ratio of at least about 4:1 relative to the copper sought to be complexed.

2. The cleaning solution of claim 1 wherein said aqueous acid solution is aqueous hydrochloric acid containing about 5% HCl by weight and which further comprises an acid corrosion inhibitor suitable therefor.

3. An acid cleaning solution for the simultaneous removal of copper and iron deposits from a ferrous metal surface while precluding redeposition of copper and the formation of a curdy adhesive precipitate at low complexor-to-copper ratios consisting essentially of:

aqueous hydrochloric acid containing about 5% HCl by weight and hexahydropriimidine-2-thione and thiourea as a mixed copper complexor dissolved therein, said mixed copper complexor being composed of 60% by weight hexahydropriimidine-2-thione and 40% by weight thiourea and being dissolved in said cleaning solution in a weight ratio of about 8:1 relative to copper sought to be removed.

4. The acid cleaning solution of claim 3 further comprising a corrosion inhibitor.

5. The method of removing copper and iron oxide containing incrustations from a ferrous metal surface while precluding redeposition of copper thereon and the formation of a curdy adhesive precipitate at low ratios of copper complexor-to-copper comprising the steps of:

(a) contacting the surface sought to be cleaned with an aqueous acid solution comprising

(a) a mixed copper complexor composed of (i) hexahydropriimidine-2-thione as a first copper complexor, said hexahydropriimidine-2-thione

being present in a concentration of from about 80% to about 20% by weight of said mixed complexor, and (ii) thiourea as a second copper complexor, said thiourea being present in a concentration of from about 20% to about 80% by weight of said mixed complexor, said mixed copper complexor being present in said solution in a weight ratio of at least about 4:1 relative to the copper sought to be removed, and

(b) an acid selected from the group consisting of hydrochloric, sulfuric, sulfamic and phosphoric acids, said acid being present in a concentration of from about 3% to about 30% by weight.

6. The method of claim 5 wherein said aqueous acid solution further comprises a suitable corrosion inhibitor.

7. The method of claim 5 wherein said acid is hydrochloric acid and wherein the method comprises the further step of agitating said aqueous acid solution in the presence of the ferrous surface to be cleaned.

8. The method of removing copper containing iron oxide incrustations from a ferrous surface while precluding the redeposition of copper on the surface sought to be cleaned and the formation of a curdy adhesive precipitate, consisting essentially of the steps of:

(a) a mixed copper complexor of (i) hexahydropriimidine-2-thione present in a concentration of about 60% by weight of said mixed complexor and (ii) thiourea present in a concentration of about 40% by weight of said mixed complexor, and

(b) hydrochloric acid containing about 5% HCl by weight, and

(c) said mixed complexor being present in said solution in a weight ratio of about 8:1 relative to the copper sought to be removed; and

agitating said mixed copper complexor in the presence of ferrous surface sought to be cleaned.

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