Copper ions are complexed by any mixture of at least two compounds represented by the general formulae:

\[ \text{and} \]

wherein \( R_1, R_3, R_5, \) and \( R_6 \) are hydrogen, alkyl radicals or alkenyl radicals; \( R_2 \) is a methylene group or an alkyl substituted methylene group; and \( R_4 \) and \( R_7 \) are hydrogen or hydroxyalkyl radicals.

In another aspect copper containing scale is removed from ferrous metal surfaces with an aqueous solution comprising the above described mixture of compounds.
COMPOSITION AND METHOD FOR REMOVING COPPER CONTAINING SCALES FROM METALS

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-to-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 are effective in initially maintaining copper in solution, they can ultimately 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 transfer 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 inclusions 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 reprecipitating and without the formation of the undesirable precipitate. Thiourea, 1,3-diethyl thiourea, ethylene 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 weight of copper complexor per unit weight of copper is used.

Other known copper complexors are hexadecyltrimine-2-thione, N-(2-hydroxyethyl)-ethylene thiourea, diethanol thiourea, and 4-methylimidazolidine-2-thione. Although this latter group of copper complexors avoids the problems of reprecipitating 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 by the present invention which provides a composition and method for complexing copper ions.

Accordingly, there has been developed in the art a one-step method for removing the aforementioned deposits whereby a removal solution capable of simultaneously removing iron oxide, copper, and copper oxide is utilized. This solution is comprised of a solvent component to dissolve, i.e., ionize, the deposit, and a second component which is 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.”

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 may be inherent in the solvent component of the solution or it may be acquired by the solution through the intervention of a substance exteriorly added or produced by the solution reaction with a portion of the deposit itself.
The copper complexing capability of the cleaning solution is surprisingly more efficient than heretofore known solutions in that the weight of copper complexor, i.e., the composition of this invention, per unit weight of copper removed, is unexpectedly lower than previously known copper complexors.

The copper complexor of this invention is the composition which consists essentially of any mixture of at least two compounds represented by the general formula:

(1)

\[
\begin{align*}
R_1 & \quad S \quad R_2 \\
R_3 & \quad N \quad C \quad N \quad R_4 \\
\end{align*}
\]

and:

(2)

\[
\begin{align*}
R_1 & \quad S \quad R_2 \\
R_3 & \quad N \quad C \quad N \quad R_4 \\
\end{align*}
\]

In formula (1) above, \(R_1, R_2, R_3, \text{and } R_4\) 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, \(R_3\) is a methylene group, i.e., a \(-CH_2-\) 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, a

\[
\begin{align*}
\left( \begin{array}{c}
CH_2 \\
CH_2 \\
\end{array} \right)^m
\end{align*}
\]

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

\[
\begin{align*}
\left( \begin{array}{c}
CH_3 \\
CH_2 \\
CH_2 \\
\end{array} \right)^n
\end{align*}
\]

group; \(R_4\) and \(R_5\) are hydrogen, a \(-CH_2CH_2OH\) group or mixtures thereof.

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

In another preferred embodiment, each of the \(R_1\), \(R_2\) groups in formula (1), and each of the \(R_3\) and \(R_4\) groups in formula (2) is hydrogen.

Compounds believed to be useful herein which are within the scope of formula (1) above include but are not limited to:

Thiourea
- Monomethyl thiourea
- 1,3-dimethyl thiourea
- Tetramethyl thiourea
- Mononethyl thiourea
- Triethyl thiourea
- Mono-n-propyl thiourea
- 1,3-di-n-propyl thiourea
- 1,1-di-n-propyl thiourea
- Monoisopropyl thiourea
- 1,3-di-isopropyl thiourea
- Monovinyl thiourea
- 1,3-divinyl thiourea
- Monoallyl thiourea
- 1-methyl-3-vinyl thiourea

1-methyl-3-allyl thiourea

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

- Thiourea
- Monomethyl thiourea
- 1,3-dimethyl thiourea
- Mononethyl 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 of this invention all of the compounds in any given mixture are within the scope of formula (1) and/or formula (2); all can be from formula (1), all can be from formula (2), or some can be from formula (1) and some from formula (2).

The maximum quantity of any single compound present in the mixed copper complexor composition of this invention is not greater than about 90, and preferably not greater than about 80, parts by weight per 100 parts by weight of the mixture with the remaining 10 to 20 parts by weight being divided among the other compounds present in the mixture. As previously stated, the mixed copper complexor composition of this invention contains at least two compounds; however, there is no presently known maximum number of such compounds which can be included in the mixture.

It is preferred, however, that any given single mixed copper complexor composition contain in the range of at least two and preferably not greater than about 10 compounds, wherein no single one of such compounds is present in the mixture in an amount greater than about 90, and preferably than about 80, parts by weight per 100 parts by weight of the mixture. In a still further preferred embodiment, the minimum quantity of any single compound is not less than 5, and preferably not less than 10, parts by weight per 100 parts by weight of the mixture. Although it is contemplated that the mixture shall contain only those compounds which are within the scope of formula (1) and/or formula (2) it is to be understood that trace quantities of materials and compounds both within and without the scope of formulas (1) and (2) can be present in the mixture.
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 oxidant present in the aqueous acid solution greatly increases the rate at which the copper becomes available to the complexor. It is believed the oxidant transforms the metallic copper to ionic copper (cuprous). 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 ions.

It has been found that the components of the present invention do not interreact chemically with each other prior to removing 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 to have a different crystalline structure than the reaction produce 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 maintained in the range of 50° 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, preferably about 4 to 8 hours.

It has also been discovered that the corrosion rates of normally inhibited hydrochloric acid on ferrous metal surfaces sought to be cleaned 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 percent hexahydropyrimidine-2-thione or 100 percent thiourea is used.

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 a surprisingly lower ratio 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 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.

The following examples are provided to further illustrate our invention, but are not to be construed to in any way limit the scope thereof.

EXAMPLES

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 Diethyli Thiourea
I — 1,3 Dimethyl Thiourea

EXAMPLE 1

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 0.006 grams 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 end point 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 I below. In Table I the total weight of complexor utilized, whether singly or in admixture, is shown to be constant at 0.5 grams for each run. In those runs where more than one complexor is indicated, then the individual complexors are present in each mixture in equal weights.

The above general rule, however, does not hold with respect to runs 12, 13, 15, 16, 37, 38, 39 and 40. Accordingly, in run 12 there are 0.4 grams A ((0.8)(0.5)=0.4), and 0.1 grams D ((0.2)(0.5)=0.2); in run 13 there are 0.3 grams A, and 0.2 grams D; in run 15 there are 0.2 grams A, and 0.3 grams D; and in run 16 there are 0.1 grams A, and 0.4 grams D. In runs 37, 38, 39 and 40 the weights of complexors A and D are constant at 0.135 grams and 0.2 grams respectively, and the weights of complexors C, F, B, and G are constant at 0.165 grams.

<table>
<thead>
<tr>
<th>RUN NO.</th>
<th>COMPLEXOR</th>
<th>CuCl–HCl</th>
<th>Cu+</th>
<th>NCL</th>
<th>H2O</th>
<th>Wt Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>0.5</td>
<td>24.2</td>
<td>0.0547</td>
<td>6.320</td>
<td>95.52</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>0.5</td>
<td>26.6</td>
<td>0.0639</td>
<td>2.277</td>
<td>97.20</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>0.5</td>
<td>20.8</td>
<td>0.0801</td>
<td>9.344</td>
<td>100.41</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>0.5</td>
<td>27.1</td>
<td>0.0987</td>
<td>6.773</td>
<td>96.39</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>0.5</td>
<td>9.1</td>
<td>0.0350</td>
<td>4.044</td>
<td>91.74</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>0.5</td>
<td>27.0</td>
<td>0.0501</td>
<td>5.777</td>
<td>94.63</td>
</tr>
<tr>
<td>7</td>
<td>G</td>
<td>0.5</td>
<td>28.6</td>
<td>0.0716</td>
<td>8.266</td>
<td>98.78</td>
</tr>
</tbody>
</table>

The wt ratio of complexor to copper is calculated for each run and is shown in the Predicted column.
Table I above clearly shows that the weight of mixed complexor 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 complexor in the mixture when acting alone.

**EXAMPLE II**

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

Each cleaning solution is then placed in a 2½-inch nominal diameter by 4-inch long mild steel pipe 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° to 1,000°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 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 II-B below.
TABLE II-A

<table>
<thead>
<tr>
<th>SOL’N NO.</th>
<th>WT*</th>
<th>COMPLEXOR</th>
<th>HCL</th>
<th>H₂O</th>
<th>CLEANING SOLUTION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gms</td>
<td>Gms**</td>
<td>Gms</td>
<td>Gms</td>
<td>HCL</td>
</tr>
<tr>
<td>1</td>
<td>247.9</td>
<td>4.4</td>
<td>12</td>
<td>233.5</td>
<td>0.968</td>
</tr>
<tr>
<td>2</td>
<td>246.94</td>
<td>1.44</td>
<td>12</td>
<td>233.5</td>
<td>0.583</td>
</tr>
<tr>
<td>3</td>
<td>247.18</td>
<td>1.68</td>
<td>12</td>
<td>233.5</td>
<td>0.68</td>
</tr>
</tbody>
</table>

* Each solution contains 0.48 ml acid corrosion inhibitors which is the reaction product of a resin amine with aldehyde and a ketone plus an acrylonic acid plus a polyethylene alkyl phenol.
** See Table II-C for the specific complexors utilized in each run.

TABLE II-B

<table>
<thead>
<tr>
<th>SOLUTION No.</th>
<th>COPPER PLATE, Gms</th>
<th>WT RATIO COMPLEXOR COPPER</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>10.1</td>
</tr>
<tr>
<td>2</td>
<td>0.24</td>
<td>6.1</td>
</tr>
<tr>
<td>3</td>
<td>0.24</td>
<td>7.1</td>
</tr>
</tbody>
</table>

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 removed from the nipple by the cleaning solution is reported in Table II-C below in terms of the weight percent of copper originally plated on the nipple. Also set out in Table II-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 complexor acting alone.

In Tables II-A and II-C the total weight of complexors utilized, whether singly or in admixture, is shown to be constant for each solution, i.e., solution 1, 2.4 grams; solution 2, 1.44 grams; solution 3, 1.68 grams. In those runs where more than one complexor is indicated, then the individual complexors 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 grams Complexor A and 1.44 grams of Complexor D; and in solution 2 there are 0.576 grams of Complexor A and 0.864 grams 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 grams and 0.96 grams respectively, and in solution 2 at 0.388 grams and 0.576 grams respectively. Complexors B, C, F, and G are present in equal weights in runs 34, 35, 36, and 37 of 0.792 grams in solutions 1 and 0.4752 grams in solutions 2.

TABLE II-C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>COMPLEXOR COMPOSITION</th>
<th>% COPPER SCALE REMOVED Solution 1 Actual</th>
<th>% COPPER SCALE REMOVED Solution 2 Actual</th>
<th>% COPPER SCALE REMOVED Solution 2 Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>100</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>-</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>97</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>100</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>65</td>
<td>39</td>
<td>39</td>
</tr>
</tbody>
</table>

* Solution 3

Table II-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 III

Cleaning solutions consisting of various solvents, corrosion inhibitors compatible with the particular solvent, water, and a mixed copper complexor consisting of 40 parts by weight thiourea per 100 parts by weight of the mixture and 60 parts by weight of hexahydroamidine-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 III below.

Each cleaning solution is then placed in a 2½-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 grams of copper and thereafter treated in a steam atmosphere at 900°F to 1,000°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 percent 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 III 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 III below in terms of the weight percent copper originally plated on the nipple.

In Example III 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 parts 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 Formic Acid

From Table III it is clearly seen that the mixed complexor of this invention is useful to remove copper in the presence of a number of solvents.

Having described our invention, that which is claimed is:

1. An aqueous cleaning solution for the removal of iron oxide and copper deposits from a ferrous metal surface consisting essentially of an acidic solvent for said deposits and a copper complexor wherein said copper complexor is a composition consisting essentially of any mixture of at least two compounds represented by the general formulae

   

   (1)

   

   (2)

   each of said compounds being present in said mixture in an amount of not greater than about 80 parts by weight per 100 parts by weight of said mixture wherein at least one of said compounds in said mixture is within the scope of said formula (1) and at least one of said compounds in said mixture is within the scope of said formula (2), and further wherein R₈, R₉, R₁₀, and R₁₁ 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; R₉ is a —CH₃— group wherein m is an integer having a value in the range of 2 to 4, a

   

   (1)

   

   (2)

   group wherein n is an integer having a value in the range of 0 to 3, or a

   

   (3)

   group; and R₈ and R₁₀ are hydrogen, a —CH₃CH₄OH group or mixtures thereof.

2. The aqueous cleaning solution of claim 1 wherein at least one of said R₈, R₉, R₁₀, and R₁₁ groups in said formula (1) is hydrogen and, at least one of said R₈ and R₁₀ groups in said formula (2) is hydrogen.

3. The aqueous cleaning solution of claim 1 wherein the pH of said solution is about 5 or less.

TABLE III

<table>
<thead>
<tr>
<th>SOLUTION COMPOSITION QUANTITY</th>
<th>CLEANING SOLUTION %</th>
<th>Complexor by wt</th>
<th>Solvent by wt</th>
<th>H₂O %</th>
<th>wt ratio</th>
<th>TREATING TEMPERATURE</th>
<th>COPPER REMOVED % by wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO.</td>
<td>Gms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>J</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
<tr>
<td>2</td>
<td>K</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
<tr>
<td>3</td>
<td>L</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
<tr>
<td>4</td>
<td>M</td>
<td>12.43</td>
<td>4.9</td>
<td>5.15</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
<tr>
<td>5</td>
<td>N</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
<td>94.78</td>
<td>10:1</td>
<td>175</td>
</tr>
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<td>7</td>
<td>P</td>
<td>11.4</td>
<td>4.9</td>
<td>4.73</td>
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<td>10</td>
<td>S</td>
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<td>11</td>
<td>T</td>
<td>12</td>
<td>4.9</td>
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<td>94.53</td>
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<tr>
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<td>V</td>
<td>24</td>
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<td>4.9</td>
<td>2.99</td>
<td>96.52</td>
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<td>150</td>
</tr>
<tr>
<td>14</td>
<td>L</td>
<td>7.5</td>
<td>0.5</td>
<td>2.99</td>
<td>96.52</td>
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<td>7.5</td>
<td>0.5</td>
<td>2.99</td>
<td>96.52</td>
<td>10:1</td>
<td>150</td>
</tr>
</tbody>
</table>
4. The cleaning solution of claim 1 wherein said mixture contains in the range of two to about 10 of said compounds.

5. The cleaning solution of claim 1 wherein the minimum quantity of any of said compounds in said mixture is about 5 parts by weight per 100 parts by weight of said mixture.

6. The aqueous cleaning solution of claim 2 wherein said integer m in said R₃ group has a value in the range of 2 to 3, and wherein said integer n has a value in the range of 1 to 2.

7. The aqueous cleaning solution of claim 1 wherein said acidic solvent is present in said solution in the range of about 0.5 to 50 percent by weight of said solution, said copper complexor is present in said solution in the range of about 0.1 to 5 percent by weight of said solution, with the remaining weight of said solution being substantially water.

8. The aqueous cleaning solution of claim 7 wherein said acidic solvent is an acid or an acidic material selected from hydrochloric acid, hydrofluoric acid, sulfuric acid, sulfamic acid, phosphoric acid, citric acid, acetic acid, gluconic acid, hydroxyacetic acid, formic acid, sodium bisulfate, sodium bifluoride, ammonium bisulfate, and mixtures thereof.

9. The aqueous cleaning solution of claim 8 wherein said at least two components are selected from thiourea, monomethyl thiourea, 1,3-dimethyl thiourea, monoethyl thiourea, 1,3-diethyl thiourea, ethylene thiourea, N-(2-hydroxyethyl)-ethylene thiourea, hexahydropyrimidine-2-thione, and 4-methylimidazoline-2-thione.

10. The aqueous cleaning solution of claim 9 wherein said acidic solvent is hydrochloric acid present in said solution in the range of about 3 to 10 percent by weight of said solution and said copper complexor is present in said solution in the range of about 0.2 to 4 percent by weight of said solution.

11. A process for removing iron oxide, and copper containing deposits from a ferrous metal surface comprising the steps of: contacting said surface with an aqueous cleaning solution comprising an acidic solvent for said deposits and a copper complexor wherein said copper complexor is a composition consisting essentially of any mixture of at least two compounds represented by the general formulæ

\[
\begin{align*}
\text{(1)} & \quad \begin{array}{c}
\text{N} \\
\text{R}_1 \\
\text{S} \\
\text{R}_2 \\
\text{R}_3
\end{array} \\
\text{(2)} & \quad \begin{array}{c}
\text{N} \\
\text{R}_1 \\
\text{O} \\
\text{R}_2 \\
\text{R}_3
\end{array}
\end{align*}
\]

each of said compounds being present in said mixture in an amount not greater than about 80 parts by weight per 100 parts by weight of said mixture wherein at least one of said compounds in said mixture is within the scope of said formulæ (1) and at least one of said compounds in said mixture is within the scope of said formulæ (2), and further wherein \( \text{R}_1, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) 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; \( \text{R}_5 \) is a \( -\text{CH}_2- \) group wherein \( m \) is an integer having a value in the range of 2 to 4, \( a \)

\[
\begin{align*}
\text{R}_4 & \quad \begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{CH}_2-\text{CH}_2
\end{array}
\end{align*}
\]

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

\[
\begin{align*}
\text{R}_4 & \quad \begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{CH}_2-\text{CH}_2
\end{array}
\end{align*}
\]

group; and \( \text{R}_4 \) and \( \text{R}_5 \) are hydrogen, a \( -\text{CH}_2\text{CH}_2\text{OH} \) group or mixtures thereof, maintaining said contacting step for a time and at a temperature sufficient for said solution to dissolve said deposits; and, thereafter, terminating said contacting.

12. The process of claim 4 wherein at least one of said \( \text{R}_1, \text{R}_2, \text{R}_3, \) and \( \text{R}_4 \) groups in said formulæ (1) is hydrogen, and at least one of said \( \text{R}_5 \) and \( \text{R}_4 \) groups in said formulæ (2) is hydrogen.

13. The process of claim 11 wherein the pH of said solution is about 5 or less.

14. The process of claim 11 wherein said mixture contains in the range of two to about 10 of said compounds.

15. The process of claim 11 wherein the minimum quantity of any of said compounds in said mixture is about 5 parts by weight per 100 parts by weight of said mixture.

16. The process of claim 12 wherein said integer \( m \) in said \( \text{R}_3 \) group has a value in the range of 2 to 3, and wherein said integer \( n \) has a value in the range of 1 to 2.

17. The process of claim 16 wherein said acidic solvent is present in said solution in the range of about 0.5 to 50 percent by weight of said solution, said copper complexor is present in said solution in the range of about 0.1 to 5 percent by weight of said solution, with the remaining weight of said solution being substantially water.

18. The process of claim 17 wherein said acidic solvent is an acid or an acidic material selected from hydrochloric acid, hydrofluoric acid, sulfuric acid, sulfamic acid, phosphoric acid, citric acid, acetic acid, gluconic acid, hydroxy-acetic acid, formic acid, sodium bisulfate, sodium bifluoride, ammonium bisulfate, and mixtures thereof.

19. The process of claim 18 wherein said acidic solvent is hydrochloric acid present in said solution in the range of about 3 to 10 percent by weight of said solution and said copper complexor is present in said solution in the range of about 0.2 to 4 percent by weight of said solution.

20. The process of claim 19 wherein said solvent is hydrochloric acid present in said solution in the range of about 3 to 10 percent by weight of said solution and said copper complexor is present in said solution in the range of about 0.2 to 4 percent by weight of said solution.

21. The process of claim 20 wherein said time is in the range of 2 to 12 hours and said temperature is in the range of 50° to 175°F.

22. The process of claim 21 wherein said cleaning solution is agitated during said contacting step.
23. The process of claim 18 wherein said at least two compounds are thiourea and hexahydropyrimidine-2-thione and said solvent is selected from hydrofluoric acid, citric acid, acetic acid, gluconic acid, hydroxyacetic acid, formic acid, sodium bisulfate, sodium bifluoro-
ride, ammonium bisulfate, and mixtures thereof.

24. The process of claim 23 wherein said ferrous metal surface is the interior surface of a boiler.
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At Column 3, lines 17 through 20, delete the formula which reads

\[
\begin{align*}
(2) & \quad R_6 \quad S \quad N \\ & \quad C \quad N \\ & \quad R_5
\end{align*}
\]

and insert therefor

\[
\begin{align*}
(2) & \quad R_6 \quad S \quad N \\ & \quad C \quad N \\ & \quad R_5
\end{align*}
\]

At Column 5, line 20, delete the word "of" and insert therefor --or--.

At Column 5, lines 33 and 34, insert the word --maximum-- between the words "known" and "quantity".

At Column 8, line 46, delete the numeral "2" (second occurrence) and insert the number --1--.

At Column 13, TABLE III, under the Column entitled "CLEANING SOLUTION" delete the title of the sub-column "H_2O By Wt" and insert --% H_2O By Wt-- therefor.

At Column 13, TABLE III, in the sub-column entitled "% H_2O By Wt" delete the figure "95.78" reflected for Solution No. 10 and insert --94.78-- therefor.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,803,042 Dated April 9, 1974

Inventor(s) John A. Knox, John A. Smith, Roy F. Stout

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At Column 14, lines 14 through 17, delete the formula which reads

(2)

\[
\begin{array}{c}
\text{R}_6 \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{R}_7 \\
\end{array}
\]

and insert therefor

(2)

\[
\begin{array}{c}
\text{R}_6 \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{R}_7 \\
\end{array}
\]

At Column 15, line 1 of Claim 7, delete the number "1" and insert "6" therefor.

At Column 15, line 2 of Claim 9, delete "components" and insert "compounds" therefor.

At Column 16, line 1 of Claim 12, delete the number "4" and insert "11" therefor.

At Column 16, line 1 of Claim 19, delete the word "acidic".

At Column 16, line 1 of Claim 20, insert "--acidic--" between the words "said" and "solvent".

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCoy M. Gibson, JR.
Attesting Officer

C. Marshall Dann
Commissioner of Patents