METHOD OF REMOVING COPPER-CONTAINING INCrustations FROM FERROUS METAL SURFACES USING AN AQUEOUS ACID SOLUTION OF AMINOALKYL THIOUREA


No Drawing. Filed Sept. 30, 1968, Ser. No. 763,957

Int. Cl. C02b 5/06; C09c 157/02; C23g 1/06

U.S. Cl. 252—87

13 Claims

ABSTRACT OF THE DISCLOSURE

Removal of copper-containing incrustations from ferrous metal surfaces accomplished in improved manner by addition of an aminomethyl thiourea such as 1-dimethylaminoethyl-3-allyl thiourea to an aqueous treating solution and subsequent treatment of ferrous metal surfaces wherein reduced sludge formation accompanies prevention of copper plating.

BACKGROUND OF THE INVENTION

This invention relates to a method of removing copper-containing incrustations from surfaces of industrial equipment wherein at least part of the associated surfaces are constituted of ferrous metals, and more particularly to a method of removing such incrustations through the addition of an aminomethyl thiourea to an aqueous medium to form a solution capable of removing the incrustations and preventing redosposition of copper as plating.

Copper-containing incrustations represent various types of copper-contaminated deposits commonly found in industrial equipment such as industrial boilers, heat exchangers and the like, associated with brass or other copper-containing metals of construction. Frequently, these also contain iron oxides from corrosion of associated ferrous metal surfaces. In some other instances, the incrustations are primarily copper present in small amounts on various areas of the ferrous metal surfaces.

The removal of these incrustations has commonly involved chemical cleaning techniques using an inhibited acid such as hydrochloric to solubilize the metal salts. However, in the presence of the ferrous metals, copper often precipitates out of solution as metallic copper and forms plating or leaves which are loosely adherent to the metal surfaces. In some instances, these are free to move about in such parts as boiler tubes and have caused dangerous conditions of reduced circulation in these tubes.

The past development of additives to reduce the problem of copper plating particularly in aqueous acid, has resulted in the use of complexing agents to retain copper in solution. Thioureas as described in U.S. 2,959,555 has been found to be effective for this purpose although, in many instances, an undesirable corrosion of metallic surfaces has accompanied its use, particularly when the treatment is carried out at high temperatures (i.e. 150° F.). The use of dialkyl thiourea such as 1,3-dithiolthiourea has reduced this problem but is often resisted in the formation of oxides associated with their copper chelates. Frequently, this sludge could not effectively be removed and limited the advantages of dialkyl thioureas.

Therefore, it is desirable to develop other agents which prevent copper plating in acid systems with a pH in the order of 0.1–4. It is also desirable to utilize these agents in other metal treating steps associated with removing oxidized copper from ferrous metal surfaces. Illustrative of the latter is a rinsing step utilized after the initial acid cleaning to increase removal of any copper contaminates present in the equipment.

In developing compositions useful for removing copper, we have discovered a class of aminomethyl thiourea which provides exceedingly satisfactory results. These compositions are characterized by improved protection of the ferrous metal surfaces during cleaning and by the essential avoidance of sludge formation. Their protection is further evident when the associated cleaning treatment is carried out at higher temperatures in the order of 150° F.

SUMMARY

Briefly, the invention is directed to an improved method of removing copper containing incrustations from ferrous metal surfaces through the addition of an aminomethyl thiourea to an aqueous solution capable of removing the incrustations and oxidized copper, followed by treating the incrustations and surfaces with the solution. The amount of the aminomethyl thiourea which is added is sufficient to prevent redeposition of copper as plating and to essentially avoid sludge formation.

DETAILED DESCRIPTION

As indicated above, the addition of aminomethyl thiourea to the aqueous medium is carried out to form the desired treating solution.

Often, the aqueous medium is an aqueous acid capable of dissolving the incrustations such as hydrochloric, phosphoric, sulfuric or sulfamic and other mineral acids; or acetic, oxalic, citric, malic, and other organic acids. In general, these solutions contain acids in the amounts of between 1 and 25 weight percent, and more normally about 2–25 weight percent. When hydrochloric acid is used, the solutions commonly contain about 4–13 weight percent of the acid.

When acid solutions are used to clean surfaces of industrial equipment, one or more corrosion inhibitors are usually incorporated into the solution. These include ethoxylated rosin amines, and various acetylenic alcohols. Normally, the corrosion inhibitors are present in small amounts to provide protection of the metallic surfaces of the equipment from attack by acid.

Another suitable aqueous medium is a water solution containing metal passivators and commonly used for rinsing acid-cleaned surfaces of industrial equipment. As previously described, the surfaces in some instances have small amounts of copper retained and the use of the aminomethyl thiourea in the water solution increases the removal of these copper contaminates.

In order that the copper be in a form which can be solubilized, an oxidant is normally present. The incrustations frequently contain iron oxide corrosion products which provide an oxidizing environment for copper when the acid acts on the incrustations. In other instances, the aqueous medium contains an oxidizing agent such as ammonium bromate which oxidizes the metallic copper.

The amount of the aminomethyl thiourea added to the aqueous medium is sufficient to prevent redeposition of copper as a plating and to avoid sludge formation. When used alone, this amount is generally in the order of about 0.1–8 percent by weight of the aqueous medium. Normally, smaller amounts are used when the solution is employed to treat previously cleaned surfaces to insure a more complete removal of copper. When acid cleaning of copper-containing iron oxide incrustations, more commonly about 2–5 weight percent of the aminomethyl thiourea provides advantageous results, although this amount depends on the degree of aminomethyl substitution of the thiourea and the extent of hydrocarbon functionality on the molecule. However, generally smaller molecular amounts of the aminomethyl thiourea can be used in an acid medium.
compared to thiourea. As a representative guideline, when 1-dimethylaminopropyl-3-methyl thiourea is utilized, about 17.6 millimoles of the aminooalkyl thiourea in a concentration of about 3 weight percent usually provides very satisfactory results, compared to about 26.3 millimoles of thiourea (concentration of about 2 weight percent).

In many acid solutions, the aminooalkyl thiourea commonly forms acid stable salts from the previously described acids. However, other acid stable salts may be formed from such agents as methyl chloride and then added to the desired solution.

The aminooalkyl thiourea of the invention is more fully described by the following formula:

\[
\text{R}_1\text{NCH}_2\text{CH}_2\text{S}\text{R}_2
\]

wherein at least one \( \text{R} \) is aminooalkyl of about 2-8 carbons, and more advantageously 3-5 carbons, at least one \( \text{R} \) is hydrogen, and the remaining \( \text{R} \)'s are aminooalkyl wherein any olefinic unsaturation is at least 2 carbons removed from the amide nitrogen. 1-dimethylaminopropyl-3-allyl thiourea is illustrative of an unsaturated thiourea with the above characteristic. More advantageously, one \( \text{R} \) is di-methylaminomethyl, two \( \text{R} \)'s are hydrogen, and the remaining \( \text{R} \) is aminooalkyl with about 1-6 carbon atoms.

The aminooalkyl thiourea of the invention has at least one hydrogen on an amido nitrogen and therefore has 1-3 aminooalkyl groups. Representative compounds are 1-dimethylaminomethyl-3-methyl thiourea, 1,3-bis(dimethylaminomethyl)-3-methyl-thiourea, 1,3,3-tris(dimethylaminomethyl) thiourea, and the like based on other amino alkyl and aminooalkyl groups illustrated above. Usually for cost and performance factors, the number of amino alkyl groups is 1-2 and preferably 1.

The amino alkyl group on the thiourea can be substituted or unsubstituted. Usually it is completely substituted with lower alkyls of about 1-4 carbon atoms such as methyl, ethyl, propyl, and the like. The connecting chain to the amido nitrogen usually contains about 2-6 carbon atoms and preferably about 3-5 carbon atoms.

Suitable groups can also be present as described above. Usually these have about 1-6 carbon atoms and are unsubstituted or contain olefinic unsaturation. Suitable groups include methyl, ethyl, propyl, butyl, hexyl, heptyl, and the like, and the corresponding unsaturated groups of 3-6 carbon atoms with the unsaturation at least 2 carbons removed from the amide nitrogen.

The invention includes compositions useful in treating metal surfaces and comprise an aqueous solution of an acid capable of dissolving copper-containing iron oxides, and a small amount of a soluble aminooalkyl thiourea or its acid stable salt. These compositions as described above are useful in removing copper-containing iron oxide incrustations from the surfaces of industrial equipment. Generally, the acid utilized is inhibited to avoid corrosion on the metal surface after the removal of the incrustation.

The following examples illustrate some of the embodiments of the invention. It is to be understood that these are for illustrative purposes only and do not purport to be wholly definitive with respect to conditions or scope.

Example I

The performance of 1-dimethylaminopropyl-3-methyl-thiourea was determined in a solution of HCl (about 5 weight percent) partially inhibited with a complex rosin amine (about 0.1 vol. percent). A synthetic scale composed of magnesium carbonate (about 0.4 weight percent), cupric oxide (about 0.1 weight percent) and cuprous chloride (about 0.1 weight percent) was added to represent conditions of use. About 17.6 millimoles of 1-dimethylaminopropyl-3-methyl-thiourea was then added to provide a concentration of about 3 weight percent.

Similar solutions with thiourea, 1,3-diethyl-thiourea, and a control (without a chelating agent) were prepared for comparison purposes.

Steel coupons of 1010 steel were immersed in each solution and tested at about 160° F. After about six hours, the coupons were examined for copper plating and weighed to determine corrosion rates. Each solution was also examined to determine sludge formation. Sludge formation was recognized by a sticky precipitate that tended to adhere to various surfaces. The results of the tests are in Table 1 below.

<table>
<thead>
<tr>
<th>Chelator</th>
<th>1-dimethyl-aminopropyl-3-methyl-thiourea</th>
<th>1,3-diethyl-thiourea</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. percent</td>
<td>........................................</td>
<td>3 3</td>
<td>3 3</td>
</tr>
<tr>
<td>Millimoles</td>
<td>........................................</td>
<td>17.6 22.7 28.3 28.3</td>
<td>134 163 286 286</td>
</tr>
<tr>
<td>Copper deposit</td>
<td>........................................</td>
<td>0 0 0 0</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>Corrosion rate (mils per year)</td>
<td>........................................</td>
<td>131 174</td>
<td>131 174</td>
</tr>
<tr>
<td>Sludge</td>
<td>........................................</td>
<td>No Yes No Yes</td>
<td>No Yes Yes Yes</td>
</tr>
</tbody>
</table>

1 None. 2 Heavy.

As demonstrated above, the 1-dimethylaminopropyl-3-methyl thiourea was more effective (based on equivalent amount) and provided improved corrosion inhibition and reduced sludge formation.

Example II

Similar solutions to those of Example I, each with a synthetic scale, were prepared with 1-dimethylaminopropyl-3-allyl-thiourea and 1,3,3-diethyl thiourea. 1010 steel coupons were immersed in each and a control. After about six hours, the extent of any copper plating and sludge formation were determined together with corrosion rates. The results are in Table 2 below.

<table>
<thead>
<tr>
<th>Chelator</th>
<th>1-dimethylaminopropyl-3-allylthiourea</th>
<th>1,3,3-diethyl-thiourea</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. percent</td>
<td>........................................</td>
<td>3 3</td>
<td>3 3</td>
</tr>
<tr>
<td>Millimoles</td>
<td>........................................</td>
<td>17.6 26.3</td>
<td>131 174</td>
</tr>
<tr>
<td>Copper deposit</td>
<td>........................................</td>
<td>0 0 0 0</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>Corrosion rate (mils per year)</td>
<td>........................................</td>
<td>131 174</td>
<td>131 174</td>
</tr>
<tr>
<td>Sludge</td>
<td>........................................</td>
<td>No Yes No Yes</td>
<td>No Yes Yes Yes</td>
</tr>
</tbody>
</table>

1 None.

The above results demonstrate that the allyl derivative of the aminooalkyl thiourea also performed well as a chelator without the formation of sludge in contrast to 1,3-diethyl thiourea.

Example III

Solutions similar to those of Example I were prepared with thiourea and 1-dimethylaminopropyl-3-methyl-thiourea. Solutions without the synthetic scale were also prepared. Corrosion rates at 82° F. were determined for each and a control using a corrosion meter equipped with 1020 steel probes. The data are in the following Table 3.

<table>
<thead>
<tr>
<th>Chelator</th>
<th>1-dimethylaminopropyl-3-methyl-thiourea</th>
<th>Thiourea</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. percent</td>
<td>........................................</td>
<td>3 2</td>
<td>3 2</td>
</tr>
<tr>
<td>Millimoles</td>
<td>........................................</td>
<td>17.6 26.3</td>
<td>131 174</td>
</tr>
<tr>
<td>Corrosion rate (mils per year), time (min.)</td>
<td>........................................</td>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20</td>
<td>1 A + B 1 A + B 1 A + B 1 A + B</td>
</tr>
</tbody>
</table>

1 Solution without synthetic scale.
2 Solution with synthetic scale.
As the above data demonstrate, the solution A with 1-dimethylaminopropyl-3-methyl-thiourea showed no accelerated corrosion in contrast to solution A with thiourea. Moreover, solution B with 1-dimethylaminopropyl-3-methyl-thiourea showed reduced corrosion compared to the control B.

While the invention has been described in conjunction with specific examples thereof, these are illustrative only. Accordingly, many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description, and it is intended to embrace all such alternatives, modifications, and variations as to fall within the spirit and broad scope of the appended claims.

We claim:

1. A method of removing copper-containing incrustations from ferrous metal surfaces without redeposition of copper, formation of sludge and with substantially reduced corrosion, which process comprises contacting said surfaces with a composition comprising aminoalkyl thiourea in an aqueous medium, said thiourea having the formula:

   \[
   \text{R-N-R'}
   \]

   wherein at least one R is aminoalkyl or dimethylaminoalkyl having from 2 to 8 carbon atoms, at least one R is hydrogen and the remaining R's are alkyl having from 1 to 6 carbon atoms or alkyl having from 3 to 6 carbon atoms with unsaturation at least 2 carbons removed from the amide nitrogen, said thiourea being present in an amount sufficient to avoid sludge formation and re-deposition of copper.

2. The method of claim 1 wherein the incrustations contain iron oxide and the amino alkyl thiourea is added to an aqueous medium containing an acid capable of dissolving the incrustations.

3. The method of claim 1 wherein the aminoalkyl thiourea is added to an aqueous medium containing an oxidizing agent for copper.

4. The method of claim 1 wherein the aminoalkyl thiourea is added in an amount of about 0.1 to 8.0 weight percent based on the aqueous medium.

5. The method of claim 1 wherein one R of the thiourea is dimethylaminodihydroxylic having from 2 to 8 carbon atoms, two R's are hydrogen, and the remaining R is alkyl having from 1 to 6 carbon atoms.

6. The method of claim 5 wherein the aminoalkyl thiourea is 1-dimethylaminopropyl-3-methyl thiourea.

7. The method of claim 1 wherein the aminoalkyl thiourea is 1-dimethylaminopropyl-3-allyl thiourea.

8. A composition for removing copper-containing incrustations from ferrous metal surfaces without redeposition of copper, formation of sludge and with substantially reduced corrosion, which composition comprises an acid capable of dissolving copper-containing iron oxide incrustations and an aminoalkyl thiourea or its acid stable salts in an amount sufficient to avoid sludge formation and re-deposition of copper, said thiourea having the formula:

   \[
   \text{R-N-C-N-R'}
   \]

   wherein at least one R is aminoalkyl or dimethylamine having from 2 to 8 carbon atoms, at least one R is hydrogen and the remaining R's are alkyl having from 1 to 6 carbon atoms or alkyl having from 3 to 6 carbon atoms with unsaturation at least 2 carbon atoms removed from the amide nitrogen.

9. The composition of claim 8 wherein one R of the thiourea is dimethylaminodihydroxylic having from 2 to 8 carbon atoms, two R's are hydrogen and the remaining R is alkyl having from 1 to 6 carbon atoms.

10. The composition of claim 9 wherein the aminoalkyl thiourea is 1-dimethylaminopropyl-3-methyl thiourea.

11. The composition of claim 8 wherein the aminoalkyl thiourea is 1,3-bis(dimethylaminopropyl) thiourea.

12. The composition of claim 8 wherein the aminoalkyl thiourea is 1,1,2-tris(dimethylaminopropyl) thiourea.

13. The composition of claim 8 wherein the acid is inhibited hydrochloric and the aminoalkyl thiourea is 1-dimethylaminopropyl-3-allyl thiourea.

References Cited

UNITED STATES PATENTS

2,959,555 11/1960 Martin ------------------ 252—149
3,000,767 9/1961 Elliott ------------------ 134—3

JOHN T. GOOLKASIAN, Primary Examiner
M. E. McCAMISH, Assistant Examiner

U.S. Cl. X.R.

134—3, 41; 252—80, 82, 149, 391; 260—552, 794