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3,579,447

**METHOD OF REMOVING COPPER DEPOSITS
FROM FERROUS METAL SURFACES USING
HYDROXYALKYL THIUREA**

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12 Claims

ABSTRACT OF THE DISCLOSURE

Removal of copper-containing incrustations from ferrous metal surfaces accomplished in improved manner by addition of a hydroxyalkyl thiourea having at least two carbon atoms in the alkyl group such as 1-hydroxyethyl-3-methyl thiourea to an aqueous treating solution and subsequent treatment of ferrous metal surfaces wherein reduced sludge formation accompanies removal of copper and the avoidance 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 constructed of ferrous metals, and more particularly to a method of removing such incrustations through the addition of a hydroxyalkyl thiourea to an aqueous medium to form a solution capable of removing the incrustations and preventing redeposition 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 complexing agents to retain copper in solution. Thiourea as described in U.S. Pat. 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. The use of dialkyl thiourea such as 1,3-diethyl thiourea has reduced this problem but often resulted in sludge formations associated with the corresponding 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.

In developing compositions useful for removing copper, we have discovered that hydroxyalkyl thioureas having at least two carbon atoms in the alkyl group provide satis-

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factory results. These compositions are characterized in acid systems by improved protection of the ferrous metal surfaces during cleaning and by avoidance of sludge formation.

SUMMARY

Briefly, the invention is directed to an improved method of removing copper containing incrustations from ferrous metal surfaces through the addition of a hydroxyalkyl thiourea having at least two carbon atoms in the alkyl group to an aqueous medium to form a solution capable of removing the incrustations and forming oxidized copper, followed by treating the incrustations and surfaces with the solution. The amount of the hydroxyalkyl thiourea which is added is sufficient to prevent redeposition of copper as plating and to essentially avoid sludges associated with some copper chelates.

The hydroxyalkyl thioureas of this invention are compositions stable in acid systems with a pH of 0.1-4. Previously unstable hydroxymethyl thiourea has been added to acid systems and found to dissociate into formaldehyde and thiourea. However, there compositions are quite dissimilar to their parent component and therefore provided very little information to us on the usefulness of stable hydroxyalkyl thioureas.

DETAILED DESCRIPTION

As indicated above, the addition of the hydroxyalkyl 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, glycolic 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 4-15 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 the acid.

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

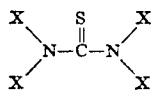
The amount of the hydroxyalkyl thiourea added to the aqueous medium is sufficient to prevent redeposition of copper as a plating and to avoid sludge formation. When used alone, this amount is generally in the order of about 0.1-8 percent by weight of the aqueous medium. Normally, smaller amounts are 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 2-8 weight percent of the hydroxyalkyl thiourea provides advantageous results although this amount depends on the degree of hydroxyalkyl substitution of the thiourea and the extent of hydrocarbon functionality on the molecule. As a representative guideline, when 1-hydroxyethyl-3-methyl thiourea is utilized, about 25 millimoles of the hydroxyalkyl thiourea in a concentration of about 3 weight percent provides very satisfactory results compared to about 26.3 millimoles of thiourea (concentration of about 2 weight percent).

In many acid solutions, the hydroxyalkyl thiourea commonly forms acid stable salts from the previously

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described acids. However, other acid stable salts may be formed from such agents as methyl chloride and then added to the solution.

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



wherein at least one X is hydroxyalkyl of about 2-5 carbons, at least one X is hydrogen, and the remaining X's are alkyl. Advantageously, the alkyl groups have 1-4 carbon atoms.

The resulting hydroxyalkyl thioureas have at least one hydrogen on the amide nitrogens and therefore 1-3 hydroxyalkyl groups. Illustrative thioureas are 1-hydroxyethyl-3-methyl thiourea, 1-hydroxyethyl-3-ethyl-thiourea, 1,1-di(hydroxyethyl)-3-methyl thiourea, 1,3-di(hydroxyethyl) thiourea, 1,3-di(hydroxyethyl)-1-methyl-thiourea, 1,3-di(hydroxyethyl)-1-ethylthiourea, 1,1,3-tris(hydroxyethyl)-thiourea, and corresponding stable, soluble hydroxyalkyl thioureas from hydroxy alkyls of 3-5 carbon atoms. Based on cost and performance considerations, hydroxyalkyl thioureas of 1-2 hydroxyalkyl groups are utilized advantageously and those having 1 hydroxyalkyl groups are preferred.

The invention includes compositions useful in treating metal surfaces and comprise an aqueous solution of an acid capable of dissolving copper-containing iron oxide incrustations and a small amount of a stable, soluble hydroxyalkyl thiourea for 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 incrustations.

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-hydroxyethyl-3-methyl-thiourea was determined in a solution of HCl (about 5 weight percent) partially inhibited with a complex rosin amine (about 0.2 vol. percent). A synthetic scale composed of magnetite (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 25.0 millimoles of 1-hydroxyethyl-3-methyl-thiourea was added to the solution to provide a concentration of about 3 weight percent.

A similar solution with about 26.3 millimoles of thiourea (about 2 weight percent) was prepared. For these solutions, tests were carried out with 1010 steel coupons at 150° F. for six hours to determine the ability of the chelator to avoid copper plating and comparisons were made with solutions containing about 3 weight percent of 1,3-diethyl thiourea. The results are in Table I below. Sludge formation was equated to the formation of a sticky thick substance.

TABLE I

Chelator	1-hydroxyethyl-3-methyl thiourea	Thiourea	1,3-diethyl-thiourea
Millimoles	25.0	26.3	22.7
Copper plating	None	None	None
Sludge	No	No	Yes

The above results demonstrate the performance of the hydroxyethyl thiourea compared to 1,3-diethyl thiourea in regard to sludge formation and its comparable performance to thiourea. While neither the solution with 1-hydroxyethyl-3-methyl thiourea or thiourea produced a

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sticky, thick sludge, it was noted that the amount of dispersed solids for the solution with hydroxyethyl thiourea was noticeably (25 estimated percent) less than for the solution with thiourea.

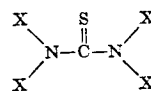
EXAMPLE II

A solution of HPO_4 (about 10 weight percent) was prepared and the synthetic scale of Example I added to it. About 3 gms. of 1,1-di(hydroxyethyl)-3-methyl-thiourea was added and tests of copper plating and corrosion were carried out on 1010 steel coupons at 160° F. The results after six hours revealed that no copper plated on the coupon surfaces and that the corrosion rate was approximately 0.2 inch per year.

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

What is claimed is:

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



wherein at least one X is hydroxyalkyl of from 2 to 5 carbon atoms, at least one X is hydrogen and the remaining X's are alkyl, said thiourea being present in an amount sufficient to avoid sludge formation and redeposition of copper.

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

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

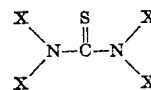
4. The method of claim 1 wherein the hydroxyalkyl thiourea is added in an amount of about 0.1 to 8.0 weight percent based on the aqueous medium.

5. The method of claim 4 wherein one X is hydroxyethyl, two X's are hydrogen, and the remaining X is alkyl with about 1-4 carbon atoms.

6. The method of claim 5 wherein the hydroxyalkyl thiourea is 1-hydroxyethyl-3-methyl thiourea.

7. The method of claim 5 wherein the hydroxyalkyl thiourea is 1-di(hydroxyethyl)-3-methyl thiourea.

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



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wherein at least one X is hydroxyalkyl of 2-5 carbon atoms, at least one X is hydrogen and the remaining X's are alkyl.

9. The composition of claim 8 wherein the hydroxyalkyl thiourea is 1-hydroxypropyl-3-methyl thiourea.

10. The composition of claim 8 wherein the hydroxyalkyl thiourea is 1,1-di(hydroxyethyl)-3-methyl thiourea.

11. The composition of claim 8 wherein the hydroxyalkyl thiourea is 1,1,3-tri(hydroxypropyl) thiourea.

12. The composition of claim 8 wherein the acid is inhibited hydrochloric and the hydroxyalkyl thiourea is 1-hydroxypropyl-3-methyl thiourea.

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U.S. Cl. X.R.

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