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METHOD OF REMOVING COPPER-CONTAINING IRON OXIDE INCRUSTATIONS FROM FERROUS METAL SURFACES USING AN AQUEOUS ACID SOLUTION OF O-AMINO THIOPHENOL

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ABSTRACT OF THE DISCLOSURE

A method of removing copper-containing iron oxide incrustations from ferrous metal surfaces through the use of an O-amino thiophenol in solution with an acid capable of dissolving the incrustations. The use of O-amino thiophenol prevents redeposition of copper as a plating, improves the removal of iron oxides in addition to copper at lower temperatures, and improves the iron oxide removing performance of thiourea in acid solutions.

BACKGROUND OF THE INVENTION

This invention relates to a method of removing copper-containing iron oxide 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 use of a soluble O-amino thiophenol in solution with an acid capable of dissolving the incrustations.

Copper-containing iron oxide incrustations represent corrosion products and soils containing oxides of iron and various compositions of copper, and are commonly found in industrial equipment such as industrial boilers, heat exchangers and the like, where brass or other copper containing metals are used in the construction. The removal of these incrustations from surfaces of industrial equipment has generally involved the use of aqueous solutions of acid such as hydrochloric to dissolve the incrustations. However, a problem of copper redeposition as plating has occurred, and it has been necessary to utilize a copper chelating thiourea to retain copper in the acid system.

While the use of thiourea in acid solutions has provided advantages over the previous techniques of copper removal, the results have not always been entirely satisfactory. In some instances, portions of the iron oxide incrustations have not been entirely dissolved without the use of higher temperatures. These temperatures have often been associated with more corrosive conditions. Therefore, it is desirable to develop other copper removal agents which work well in high acid systems with a pH in the order of 0.1–4.

In developing compositions for use in high acid systems for preventing redeposition of copper as plating, we have discovered that a class of aromatic compounds considerably different from the thioureas, provides exceedingly satisfactory results. In addition, these compounds also exhibit advantageous performance in comparison with thiourea, and also even aid the performance of thiourea.

The aromatic compounds are amino aromatic thiols with the amino and thio groups in an ortho relationship. Generally, they are characterized as O-amino thiophenols and usually have from 1–2 aromatic groups in the aromatic nucleus.

SUMMARY

Briefly, the invention is directed to a method of removing copper-containing iron oxide incrustations from ferrous metal surfaces by adding to an aqueous solution of an acid capable of dissolving the incrustations, a soluble O-amino thiophenol in a sufficient amount to prevent redeposition of copper as a plating, and treating the surface with the resultant solution. The invention also is directed to compositions comprising an aqueous solution of an acid capable of dissolving copper-containing iron oxide incrustations and a small amount of a soluble O-amino thiophenol or acid-stable salt thereof and to compositions comprising a combination of an O-amino thiophenol or acid-stable salt and a thiourea or substituted thiourea.

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In general, the acid solutions are prepared from mineral acids such as hydrochloric, phosphoric, sulfuric or sulfamic, or organic acids such as acetic, oxalic, citric, malic or glycolic. In general, these solutions contain acids in the amounts of between 2 and 25 weight percent. When hydrochloric acid is used, the solutions commonly contain about 4–15 weight percent of the acid.

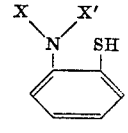
Commonly, when the acid solutions are used to clean surfaces of industrial equipment, one or more corrosion inhibitors are incorporated into the solution. These include various amines such as ethoxylated rosin amines and various acetylenic alcohols. Normally, the corrosion inhibitors are present in small amounts to provide protection of the metallic surfaces of the equipment from attack by the acid. In some instances, an oxidant such as a bromate is present to improve conditions for oxidizing any metallic copper.

For purposes of this invention, the acid solution also contains a soluble O-amino thiophenol or acid-stable salt in a sufficient amount to prevent redeposition of copper as a plating. When used alone, this amount is generally in the order of about 0.5–8 percent by weight of the final solution. Normally, the amount is determined on the basis of copper present to provide at least a 2:1 weight ratio to provide essentially complete copper removal. When used in combination with a thiourea or substituted thiourea, the amount of O-amino thiophenol or salt is adjusted accordingly to enhance the performance of the thiourea. Commonly, the ratio of O-amino thiophenol to thiourea is in the order of .5–5.0:1 on a weight basis.

Acid stable salts are compositions derived from the O-amino thiophenol and an acid or simple salt. Usually, the acid is that utilized to dissolve the incrustations. Other salts are those formed from methyl chloride and other simple salts which are stable in the acid systems.

The O-amino thiophenol is descriptive of aromatic compounds having 1–2 aromatic rings wherein the amino and thio groups are in an ortho relationship. These compositions can be unsubstituted or substituted with substituents which do not intefere with the desired action of the thiophenol. Suitable groups include alkyls of 1–12 carbon atoms, halo, amino, and the like. In some instances such as with the thionaphthols, it is desirable to have additional amino and thio groups on the aromatic nucleus to improve solubility and performance of the compounds. Illustrative of these compositions are 1-amino-2-thio-5-amino-6-thionaphthol and the like.

Preferable O-amino thiophenols of the present invention are represented by the following formula:



where X and X' are independently selected from the group consisting of hydrogen and alkyl of from 1–4 carbon atoms. Suitable substituents include alkyls of 1–4 carbon atoms as illustrated by such amino groups as dimethylamino, propylmethylamino, butylmethylamino,

monomethylamino, monoethylamino, monobutylamino, and the like. Advantageously, the amino group is unsubstituted or monosubstituted and preferably is unsubstituted.

Usually, the action of the O-amino thiophenol results in a loose flocculent which is easily removable. Its removal may be assisted by means of suspending aids such as emulsifiers or through the use of a pumping means to provide sufficient velocity for the suspending action although these are ordinarily not necessary. Suitable emulsifiers include those associated with the use of thioureas as disclosed in U.S. 3,188,292 and U.S. 3,294,695.

The following examples illustrate some of the embodiments of this 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

Two hydrochloric acid solutions were prepared and inhibited with a complex amine. Each solution consisted of approximately 100 ml. of 5 weight percent hydrochloric acid with approximately 0.2 weight percent of the amine. A synthetic scale representing copper-containing iron oxide incrustations and composed of approximately 1.3 g. of magnetite and 0.31 g. of cuprous chloride was added to each acid solution. Approximately 4.0 g. of O-amino thiophenol was added to one solution and the other was considered to be the control.

The temperature of each solution was raised to approximately 150° F. and a 1010 steel coupon was immersed in each solution. After approximately six hours, the solution containing the O-amino thiophenol exhibited no copper plating on the steel coupon and a loose flocculent precipitate had been formed. The control solution exhibited a heavy coating on the coupon with evidence of copper and only part of the synthetic scale had been dissolved.

Example II

Two beakers were filled with approximately 100 ml. each of a 5 weight percent hydrochloric acid solution inhibited with approximately 0.2 weight percent of a complex amine. The synthetic scale composed of approximately 0.4 g. magnetite, 0.1 g. of cuprous chloride, and 0.1 g. of cupric oxide was added to each solution. Various combinations of O-amino thiophenol, thiourea and a substituted thiourea were added to various solutions as shown in Table 1 below. Steel corrosion coupons of 1010 steel were immersed in the solutions and the temperature was maintained at approximately 150° F. for about six hours. The results are also shown in Table 1 below.

TABLE 1

No.	Copper removal agents[1]	Wt. percent	Coupon appearance	Solution appearance
1		0	Heavy copper coating.	Scale not completely dissolved.
2	A	1	Clean	Slight flocculent-scale dissolved.
	B	2		
3	A	2	----do----------	Do.
	B	2		
4	A	2	----do----------	Do.
	C	2		
5	D	1	-----do----------	Scale not completely dissolved.
6	D	2	-----do----------	Do.

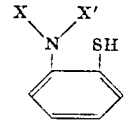
[1] A—O-amino thiophenol; B—1-hydroxyethyl-3-methylthiourea; C—1,1-dihydroxyethyl-3-methylthiourea; D—Thiourea.

The above results for Examples I–II demonstrate that the use of O-amino thiophenol alone or in combination with a substituted thiourea resulted in the magnetite scale being completely dissolved; whereas with unsubstituted thiourea alone, the scale was not completely dissolved. In Example I approximately 4.0 gm. (4 weight percent) of O-amino thiophenol was utilized with 0.31 gm. of cuprous chloride. In Example II, the amounts of the chelators were reduced as a result of reduced copper present.

While the invention has been describd 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 iron oxide incrustations from ferrous metal surfaces without redeposition of copper as a plating which process comprises contacting said surfaces with a composition consisting of an aqueous solution of an acid capable of dissolving the incrustations and a soluble O-amino thiophenol or its acid stable salt in an amount sufficient to prevent redeposition of copper, said thiophenol having the formula:



where X and X' are independently selected from the group consisting of hydrogen and alkyl of from 1 to 4 carbon atoms.

2. The method of claim 1 wherein the amount is approximately 0.5–8.0 weight percent based on the initial solution of acid.

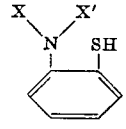
3. The method of claim 1 wherein said acid solution includes a small amount of a copper-chelating thiourea selected from the group consisting of thiourea and hydroxyalkyl thiourea.

4. The method of claim 1 wherein said method includes forming a solution of said acid containing an emulsifier.

5. The method of claim 1 wherein said thiophenol is O-methylamino thiophenol.

6. The method of claim 1 wherein said thiophenol is O-amino thiophenol.

7. A composition for removing copper-containing incrustations from ferrous metal surfaces without redeposition of copper as a plating, which composition comprises an aqueous solution of an acid capable of dissolving the incrustations and a copper-chelating thiourea selected from the group consisting of thiourea and hydroxyalkyl-thiourea in combination with an O-amino thiophenol having the formula:

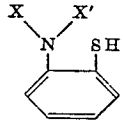


where X and X' are independently selected from the group consisting of hydrogen and alkyl of from 1–4 carbon atoms.

8. The composition of claim 7 wherein the substituted thiourea is 1-hydroxyethyl-3-methyl thiourea.

9. The composition of claim 7 wherein the composition contains 1–4 weight percent of thiourea.

10. A composition for removing copper-containing incrustations from ferrous metal surfaces without redeposition of copper as a plating, which composition comprises an aqueous solution of an acid capable of dissolving the incrustations and a soluble O-amino thiophenol or its acid stable salt in an amount sufficient to prevent redeposition of copper, said thiophenol having the formula:



where X and X' are independently selected from the group consisting of hydrogen and alkyl of from 1–4 carbon atoms.

11. The composition of claim **10** wherein the amount is approximately 0.5–8.0 weight percent based on the aqueous solution.

12. The composition of claim **10** wherein said acid solution includes a small amount of a copper-chelating thiourea selected from the group consisting of thiourea and hydroxyalkyl thiourea.

13. The composition of claim **10** wherein the aqueous solution contains an oxidant for copper.

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