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[54] **COMPOSITION AND PROCESS FOR THE REMOVAL OF COPPER DURING ACID CLEANING OF FERROUS ALLOYS**

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[51] Int. Cl.²..... **C02B 5/06**

[58] Field of Search 252/149, 180, 80; 210/58; 134/41, 3

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[57] ABSTRACT

A composition and process for the removal of copper compounds during acid cleaning operations of ferrous alloy surfaces wherein a liquid, easily soluble composition is incorporated in the cleaning solution, said composition being the reaction product of (1) an aliphatic or cycloaliphatic aldehyde, (2) an hydroxyethyl amine and (3) thiourea.

22 Claims, No Drawings

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COMPOSITION AND PROCESS FOR THE REMOVAL OF COPPER DURING ACID CLEANING OF FERROUS ALLOYS

BACKGROUND OF THE INVENTION

1. Field of The Invention

The present invention relates to a composition and process for the removal of copper encrustations on metallic surfaces during acid cleaning operations.

2. Description of the Prior Art

One of the most commonly encountered problems in industrial cleaning of ferrous alloys is that of removing iron oxide and other scale deposits from the surface of ferrous equipment such as those incorporated in steam generators, heat exchangers, boilers, piping and similar process equipment. These deposits contain iron oxide, often combined with other inorganic constituents such as calcium carbonate, magnesium oxide, copper oxide and the like. Complete removal of copper compounds from such encrusted surfaces is important, but difficult, since the iron present on the surface acts as a chemical reducing agent causing plating out of any temporarily dissolved copper, and thus forming a copper coating on the ferrous alloy surface. Such copper plating is very undesirable because it provides a highly cathodic area which furthers corrosive attack of any uncoated ferrous alloy surface after the equipment is returned to normal service. For example, in a high temperature boiler, the presence of a copper-coated cathodic area can cause greatly accelerated corrosion, pitting and devastating failure of nearby ferrous structures.

The removal of copper compounds during cleaning of ferrous equipment with acid solutions had been attempted to those skilled in the art using a number of compositions and processes. For example, hydrochloric acid, sulfamic acid, hydroxy acetic acid or mixtures of hydrochloric acid with other acidic constituents, corrosion inhibitors and wetting agents, are commonly used for removing and dissolving such scaling deposits containing copper compounds. Another method of overcoming the problem of copper encrustation is presented in U.S. Pat. No. 2,959,555 wherein it is disclosed that the inclusion of suitable amounts of thiourea and lower alkyl-substituted thioureas causes the copper to remain in solution in the hydrochloric acid cleaning compound as a metal complex, allowing the complexed copper in solution to be completely washed out with the acid or spent acid. Although this method does permit the removal of copper compounds, iron oxide and other scale constituents, it has been found to be somewhat unsatisfactory in commercial applications. For example, thiourea has very limited solubility in water as well as in hydrochloric acid. Its alkyl derivatives are known to be even less soluble. Putting these solid products into solution in an acid during the cleaning process becomes a somewhat difficult, tedious and time-consuming operation involving solids handling in open solution tanks, stirring or recirculation of acid to effect solution and, sometimes, even heating of the acid. In addition, thiourea and its lower alkyl derivatives generally interfere with the action of corrosion inhibitors commonly used in the acid by those skilled in the art to prevent attack on the metallic alloy structure underlying the iron oxide and other encrustations. Moreover, the cost of the corrosion inhibitor required is a very significant one, and when thiourea is used even greater

quantities of inhibitor must be employed, thus substantially increasing the cost of the cleaning operation.

I have now discovered that the disadvantages encountered in the use of thiourea can now be completely overcome by incorporating in the cleaning solution a copper complexing agent consisting essentially of (1) thiourea, (2) an aldehyde selected from the class consisting of aliphatic and cycloaliphatic aldehydes and (3) an hydroxyethyl amine, all as hereinafter disclosed.

The present invention provides a composition and process for the removal of copper-containing compounds during acid cleaning of ferrous surfaces. Specifically it provides for the use in an acidic solution employed during the cleaning of ferrous surfaces a copper-complexing composition which is in the form of a readily handled liquid and is easily soluble in water and acidic solutions. Moreover, this composition is very economical and has been found not to have an adverse effect on the action of corrosion inhibitors used in the cleaning solution. In fact, the composition herein described has been found to reinforce the effects of corrosion inhibitors under some conditions, and, in general, to have fewer negative effects on commonly used inhibitors than does thiourea or its lower alkyl derivatives alone.

It is therefore an object of the present invention to provide a process for the removal of copper depositions on ferrous alloys.

It is also an object of the present invention to provide a composition for the removal of copper depositions and encrustations during cleaning operations of ferrous alloy surfaces of water treatment apparatuses, piping and the like.

It is a further object of the present invention to provide a copper complexing agent for use during industrial cleaning operations.

Other objects and advantages in the use of the present composition and process will be apparent from the description, examples and claims which follow.

SUMMARY OF THE INVENTION

A composition and process for the removal of copper compounds during acid cleaning operations of ferrous alloy surfaces wherein a liquid easily soluble copper complexing agent is incorporated in the cleaning solution, such agent being the reaction product of (1) an aliphatic or cycloaliphatic aldehyde, (2) an hydroxyethyl amine and (3) thiourea.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The composition of the present invention may be described in its broadest form as the reaction product of:

- a. An aliphatic or cycloaliphatic aldehyde having five carbon atoms or less;
- b. An amine having an hydroxyethyl or substituted hydroxyethyl group attached to an amino nitrogen atom; and
- c. Thiourea.

Although the exact formula for the composition of the present invention is not known, solubility properties and reactivity suggest that the composition may be classified as nitriloethoxymethylene thiocarbamates. The multiplicity of possible formulae for compositions of this class make classification impossible, so I prefer to describe the composition in terms of suitable reactants and molar proportions of each.

In order to obtain compositions having the desired solubility and utility, the ratio of the number of carbon atoms in aliphatic or cycloaliphatic substituents in my composition to the number of polar groups therein, such as amino, aldehyde and hydroxyl, should remain below about 6-to-1 and, preferably, below about 3-to-1. Further, I have found that suitable compositions result when the molar equivalent of aldehyde reactant used is from about 1.0 to about 2.5 times the number of moles of thiourea and when the molar equivalent of hydroxy present in the hydroxyethyl amine reactant is also from about 1.0 to about 2.5 times the number of moles of thiourea. Additionally, the molar equivalent of hydroxy in the hydroxyethyl amine reactant must be about equal to the molar equivalent of aldehyde in the aldehyde reactant.

Aldehydes suitable for use in the synthesis of the present composition include the aliphatic and cycloaliphatic aldehydes containing five carbon atoms or less, such as formaldehyde, trioxane, paraformaldehyde, acetaldehyde, propionaldehyde, furfural, glyoxal, glutaraldehyde, acrolein, caproaldehyde and the like. Especially preferred are those aliphatic and cycloaliphatic aldehydes containing three carbon atoms or less per aldehyde group, such as formaldehyde, acetaldehyde, propionaldehyde, glyoxal, acrolein and the like. Polymeric forms of these lower aldehydes, such as paraformaldehyde and trioxane, can also be utilized since they will serve as a source of monomeric aldehyde under normal reaction conditions. Other polymers such as paraldehyde and metaldehyde may also be successfully utilized.

Amines suitable for use in preparing the present composition are the aliphatic amines having at least one hydroxyethyl or substituted hydroxyethyl group attached to the amino nitrogen. The preferred amine reactant should not contain so many hydrocarbon constituents as to render the final composition insoluble or difficultly soluble in water or acidic cleaning solutions. Preferred amines will contain less than about seven carbon atoms per amino nitrogen atom and especially preferred reactants will contain only two or three carbon atoms per amino nitrogen atom. Examples of suitable amine reactant include 2-hydroxypropylamine, monoethanolamine, diethyl monoethanolamine, methyl diethanolamine, triethanolamine, hydroxyethylethylene diamine, di-2-hydroxypropylamine and the like.

The reaction of the aldehyde and amine reactants with thiourea may be carried out simply by mixing the reagents and warming slightly while stirring until the solid thiourea disappears and a homogeneous, liquid product is obtained. Usually, however, it will be preferred to incorporate some water into the reaction mixture and to add an organic or inorganic acid in an amount at least equivalent to about one-fifth of the amine present. The acid may be added before, during or near the end of the reaction period. Suitable acids for use with the present composition include acetic acid, hydrochloric acid, sulfuric acid and phosphoric acid in concentrations of from between about 5% and about 25%. The use of acetic acid is preferred.

Completion of reaction is generally marked by dissolution of the thiourea and formation of a clear, homogeneous liquid of a deep yellowish or reddish color. Typically, the temperature is brought to about 90°C and held for one hour to effect reaction although with higher boiling or less reactive reagents, the tempera-

ture may be raised above this point, as, for example, to 150°C.

The following examples further illustrate the preparation of the present composition.

EXAMPLE I

76 grams of thiourea and 50 grams of thiethanolamine were placed in a 500 ml. three-neck flask fitted with stirrer, reflux condenser, thermometer and exterior heating mantle. While stirring at room temperature, 210 grams of 30% aqueous glyoxal were added over a period of one hour. 20 grams of acetic acid were then added over a 10-minute period during which time the temperature rose to about 35°C. The heating mantle was then activated and the temperature increased to 95°C and held for 1 hour. The resulting composition was a viscous red oil, soluble in water, 5% hydrochloric acid and dilute alkali.

EXAMPLE II

76 grams of thiourea and 50 grams of triethanolamine were combined in a flask equipped as in Example I. While stirring at room temperature, 81 grams of 37% formalin solution (methanol-free) were quickly added to the mixture in the flask. 25 grams of acetic acid were then added over a 30-minute period during which the temperature rose to about 40°C. The temperature was then raised to 110°C and held for 30 minutes. The resulting clear, red oil was soluble in water and 5% hydrochloric acid. The pH of a 10% solution of this composition in distilled water was 5.4.

EXAMPLE III

104 grams of hydroxyethylethylenediamine were substituted for the triethanolamine used in Example II. The resulting red oil dissolved readily in water and a 10% solution thereof had a pH of about 8.5. This composition was also readily soluble in both acidic and alkaline solutions.

EXAMPLE IV

76 grams of thiourea, 150 grams of furfural and 100 grams of water were combined in a 1-liter flask equipped as in Example I. 100 grams of isopropanolamine were then slowly added to the flask contents while stirring. A small exotherm was noted. 75 grams of 10% aqueous hydrochloric acid were then added over a 1-hour period. The temperature spontaneously rose to about 50°C and was then raised to 105°C by external heating. It was held at this temperature for about 25 minutes. The resulting composition resembled that of Example III in physical properties.

EXAMPLE V

61 grams of thiourea, 74 grams of monoethanolamine and 40 grams of water were placed in a flask as in Example I. While stirring this mixture, 66 grams of chilled acetaldehyde were added in 5 gram increments. The incremental additions took place over one hour during which a mild exothermic reaction raised the temperature from 25°C to 32°C. 16 grams of acetic acid were then added to the reactant and heat slowly applied in order to raise the temperature to 114°C. The reactants were stirred and held at this temperature for 90 minutes. The resulting red oil composition was very soluble in water and acids in aqueous solutions.

EXAMPLE VI

100 grams of 10% aqueous hydrochloric acid were substituted for the acetic acid in Example V. The resulting composition was prepared as in Example V and was found to be quite soluble in water and acids in aqueous solutions.

EXAMPLE VII

61 grams of thiourea, 74 grams of monoethanolamine and 40 grams of water were reacted in a flask as in Example I. The flask was held in a water bath at a temperature of about 25°C. While stirring the reaction in the flask, 220 grams of 40% aqueous glyoxal were added to the reactants incrementally over a period of 20 minutes. The water bath was replaced by a heating mantle and the flask contents were then brought to and held at 85°C for 1 hour and 25 minutes. The product was a mobile red oil, readily soluble in water and aqueous acids.

EXAMPLE VIII

The following test solution was prepared:

CuCl		0.128%
Crude Pyridine	Corrosion Inhibitor	0.4%
HCl		5.0%
Water to make		100.0%

Steel coupons measuring about 1½ inch × ½ inch × ⅛ inch were immersed in 50 ml. of the above solution containing a known amount of the present composition made according to the above Examples. The bottles containing the solution and coupon were held in a water bath at 70°C for 3 hours. The solutions were observed immediately after adding the composition and the coupons were removed and examined after the test period. The results of these tests using the composition of the present invention are given in Table 8 below, along with the results obtained using only thiourea.

Table 8

Product Used	Concentration in Test Solution	Appearance Of Solution	Appearance of Coupon After 3 Hours. at 70°C
Example 2	1.8%	slightly cloudy	slight copper deposit
2	3.0	clear	no deposit of copper
Example 4	2.0	flocculant precipitate	some deposit of copper
4	3.2	trace precipitate	trace of copper
Example 5	1.2	fine fluffy precipitate	heavy copper
5	1.6	trace of precipitate	no copper
5	2.0	very clear	no copper
Thiourea	0.6	flocculant precipitate	moderate copper deposit
	0.8	clear	no copper

EXAMPLE IX

The present Example demonstrates the effects of varying concentrations of thiourea and of the product of Example VI on the corrosion rate of mild steel exposed to a hydrochloric acid solution. The solution used was 5.6% aqueous hydrochloric acid in which was dissolved 2.0% iron oxide, 0.08% cuprous oxide, and 0.4% crude alkyl pyridine corrosion inhibitor.

Weighed steel coupons were exposed for four hours at 160°F to aliquots of this solution containing various concentrations of thiourea and of the product of Exam-

ple VI. The coupons were reweighed after test exposure and chemical removal of any deposited copper. Corrosion rates were computed from the weight loss, time of exposure and coupon dimensions and are presented below in Table 9 (in unites of "mils per year" which is defined as thousandths of an inch penetration per year (MPY)).

Table 9

Corrosion Rate of Weighed Steel Coupons in Hydrochloric Acid Solution		
Copper Complexing Agent	Concentration of Agent, %	Corrosion Rate, MPY
None	—	2,060
Thiourea	0.25	800
D.O.	1.00	1,040
D.O.	2.00	2,170
Product of Example VI	0.25	760
D.O.	1.00	800
D.O.	2.00	510

These results demonstrate the increasingly beneficial effect of the additive, composition and process of the present invention in reducing the corrosion rate as higher concentrations are employed. Thiourea, in contrast, shows a corrosion rate slightly exceeding the blank ("None") rate when present at a 2.0% concentration. Normal commercial use concentrations may equal or exceed 2.0% in many cases.

EXAMPLE X

Actual application of the present invention in an industrial cleaning operation is relatively simple and is exemplified by the log of a boiler cleaning operation. The boiler to be cleaned was a Babcock and Wilcox fire tube model having a volumetric capacity on the water side of 15,000 gallons and constructed of carbon steel. Cleaning of the heater was necessary to remove iron oxides, silica, copper oxides and other organic and inorganic scale constituents. The boiler was first given an

alkaline wash by circulating through the tubes and drum while firing to a temperature of about 190°F, 15,000 gallons of an aqueous solution containing 300 gallons of 50% caustic soda, 1,800 pounds of soda ash and 5 gallons of hydrazine. This solution was circulated for 15 hours after which heating was stopped and the spent solution drained and discharged. The bottom headers and drum were flushed with water to remove alkaline solution and loose deposits. An acid solution was then prepared containing 2,100 gallons of 32% commercial hydrochloric acid, 990 pounds of ammonium bifluoride, 100 pounds of citric acid, 55 gal-

lons of crude alkyl pyridine, 1200 pounds of the product of Example V, and sufficient water to bring the total volume to slightly over 15,000 gallons. The boiler was then filled with the acid solution which was heated to 190°F and circulated for 6 hours. Firing was stopped and the spent acid was drained from the boiler after which the heater was filled with a soda ash neutralizing solution containing 100 pounds of soda ash per 1,000 gallons of water. This solution was then drained. The boiler was blown down with dry nitrogen preparatory to being put back in service.

An analysis of the spent acid indicated that the quantity of scale constituents removed in the true solution was as follows:

Silica	53.5	pounds
Copper	107.0	pounds
Iron	1,759	pounds

Visual inspection of the interior boiler surface showed a greyish metallic surface which was free of scale deposits. The boiler surface was also rust resistant.

The ability of the present composition to hold copper in solution is clearly shown by the above results. In comparing amounts required for optimum results it should carefully be noted that the products of Examples I through VII are diluted with water and are not 100% active. Thiourea, in contrast, is a 100% active solid.

Much of the utility of the present composition is attributable to the fact that it is an aqueous solution of high activity which can be pumped, poured, mixed and easily dissolved in acidic cleaning solutions.

The amount of the composition which is required for holding copper in solution varies with the amount of copper in any given system to be cleaned and with the particular composition to be used. Generally speaking, an amount of the composition which will provide from about 1.8 to about 2.0 pounds of sulphur for every pound of copper ion in the system will achieve very satisfactory results. In contrast, where thiourea is used, an amount sufficient to provide at least 2.5 pounds of sulphur is generally necessary to prevent precipitation and copper deposition. Thus, an obvious advantage in the use of the present composition is readily apparent.

Since the amount of copper in the system strongly affects the required amount of the present composition, it becomes very important to make careful analysis of the scale and impurities in the system to be cleaned and to estimate as carefully as possible the amount of copper present. This is frequently difficult to accurately ascertain. It is preferable to use slightly more of the present composition than might be indicated by preliminary testing and the like. Under some abnormal conditions, it may desirable to utilize amounts of the present composition sufficient to provide up to 5 pounds of sulphur per pound of copper. Use of too little of the composition results in the formation of insoluble complexes of copper and composition. In such mixtures, plating out of copper may still be prevented. However, unless high fluid velocities and good turbulence are present during draining of the acid cleaning solution, subsequent flushing and neutralization, some precipitate may be left in the system to act as a source of copper in the future operations. For this reason it is desirable to use sufficient amounts of the present invention in order to

prevent formation of any copper-containing cloud or precipitate.

The use of more of the present composition than is required by the copper present in the system is, of course, undesirable from an economic viewpoint. Still further, the use of increased amounts of the present composition will sometimes also require the addition of more corrosion inhibitor, which further increases cost. This is particularly true with thiourea which has a generally negative effect on inhibitor performance. The composition of the present invention, in contrast, has less effect on inhibition and does, in some instances, actually improve inhibitor performance.

Although the invention has been described in terms of specified embodiments which are set forth in detail, it should be understood that this is by illustration only and that the invention is not necessarily limited thereto, since alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications are contemplated which can be made without departing from the spirit of the described invention.

I claim:

1. An additive for use in compositions for the removal of copper encrustations encountered during acid cleaning operations of ferrous alloy surfaces consisting essentially of the reaction product of

a. an aliphatic or cycloaliphatic aldehyde having five carbon atoms or less;

b. an amine having an hydroxyethyl or substituted hydroxyethyl group attached to an amino nitrogen atoms; and

c. Thiourea,

the ratio of carbon atoms in the aliphatic or cycloaliphatic substituents to the number of polar groups therein being no greater than about 5-to-1, the molar equivalent of aldehyde being between about 1.0 and about 2.5 per mole of thiourea, the molar equivalent of hydroxy present in the amine being from about 1.0 to about 2.5 times the number of moles of thiourea, and the molar equivalent of hydroxy being equal to the molar equivalent of aldehyde.

2. The additive of claim 1 wherein the ratio of carbon atoms in the aliphatic or cycloaliphatic substituents to the number of polar groups therein is below about 3-to-1.

3. The additive of claim 1 wherein the aldehyde is selected from the class consisting of formaldehyde, trioxane, paraformaldehyde, acetaldehyde, propionaldehyde, furfural, glyoxal, glutaraldehyde, acrolein and caproaldehyde.

4. The additive of claim 1 wherein the aldehyde is selected from the class consisting of paraformaldehyde, paraldehyde and metaldehyde.

5. The additive of claim 1 wherein the amine contains less than about 7 carbon atoms per amino nitrogen atom.

6. The additive of claim 1 wherein the amine contains three carbon atoms per amino nitrogen atom.

7. The additive of claim 1 wherein the amine contains about two carbon atoms per amino nitrogen atom.

8. The additive of claim 1 wherein the amine is selected from the class consisting of 2-hydroxypropylamine, monoethanolamine, diethyl monoethanolamine, diethanolamine, methyl diethanolamine, triethanolamine, hydroxyethylene diamine and di-2-hydroxypropylamine.

9. A composition for the removal of copper compounds during acid cleaning operations of ferrous alloy surfaces consisting essentially of an aqueous solution of an acid and the additive of claim 1, the ratio of acid in said composition to the amine in the additive being at least as high as about 1-to-5 by volume.

10. The composition of claim 9, wherein the acid is an organic acid.

11. The composition of claim 9 wherein the acid is an inorganic acid.

12. The composition of claim 9 wherein the acid is selected from the class consisting of acetic, hydrochloric, sulfuric and phosphoric.

13. The composition of claim 9 wherein the acid is acetic.

14. A process for the removal of copper encrustations on ferrous alloy surfaces comprising the steps of:

a. Contacting the ferrous surface with an aqueous solution of (1) the additive of claim 1 in an amount sufficient to provide from about 1.8 to about 5.0 pounds of sulphur for each pound of copper ion, and (2) an acid selected from the class consisting of acetic, hydrochloric, sulfuric and phosphoric, the amount of acid in said solution being a ratio to the amine in the additive of at least as high as about 1-to-5 by volume; and

b. Maintaining contact with the said ferrous surface by the said aqueous solution for a time sufficient to substantially solubilize the said copper encrustation.

15. The process for the removal of copper encrustations on ferrous alloy surfaces comprising the steps of:

a. Contacting the ferrous surface with an aqueous solution of an additive consisting essentially of the reaction product of (1) an aldehyde having five carbon atoms or less selected from the class consisting of aliphatic and cycloaliphatic aldehydes, (2) an amine having a hydroxyethyl or substituted hydrox-

yethyl group attached to an amino nitrogen atom, and (3) thiourea, said additive being present in an amount sufficient to provide from about 1.8 to about 5.0 pounds of sulphur for each pound of copper present, and an aqueous acidic solution comprising an acid selected from the class consisting of acetic, hydrochloric, sulphuric, and phosphoric acids; and

b. Maintaining contact with said ferrous surface by the said aqueous acidic solution having present therein the said additive for a time sufficient to solubilize substantially all of said encrustation.

16. The process of claim 15 wherein the aldehyde is selected from the class consisting of formaldehyde, trioxane, paraformaldehyde, acetaldehyde, propionaldehyde, furfural, glyoxal, fluteraldehyde, acrolein and caproaldehyde.

17. The process of claim 15 wherein the aliphatic or cycloaliphatic reactant contains less than four carbon atoms per aldehyde group.

18. The process of claim 15 wherein the aldehyde is selected from the class consisting of paraformaldehyde, trioxane, paraldehyde and metaldehyde.

19. The process of claim 15 wherein the amine contains less than about seven carbon atoms per amino nitrogen atom.

20. The process of claim 15 wherein the amine contains 3 carbon atoms per amino nitrogen atom.

21. The process of claim 15 wherein the amine contains about two carbon atoms per amino nitrogen atom.

22. The process of claim 15 wherein the amine is selected from the class consisting of 2-hydroxypropylamine, monoethanolamine, diethyl monoethanolamine, diethanolamine, methyl diethanolamine, triethanolamine, hydroxyethylethylene diamine and di-2-hydroxypropylamine.

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