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REMOVAL OF COPPER CONTAINING SCALE FROM FERROUS SURFACES

Fred N. Teumac, Charlotte, N.C., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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The invention relates to a method and composition for the cleaning of ferrous metal surfaces having a copper bearing scale, deposit or encrustation thereon.

The word "deposit" as used hereinafter is meant to include oxide encrustation developed on the surface of the metal as well as deposits of iron oxide transferred from other sites and also including hardness deposition from solution.

It is known to clean ferrous metal surfaces with an aqueous solution of citric acid having an acid pH. However, acidic cleaning solutions are generally considered to be somewhat undesirable as these can cause permanent damage to ferrous metal equipment. Also, it appears to be necessary to adjust the pH of the citric acid solution to an alkaline pH in order to passivate the surface of the ferrous metal before completion of the cleaning operation. According to U.S. Patent No. 3,248,269, it is necessary to bring a citric acid solution to an alkaline pH in order to dissolve copper or copper oxides. Such neutralization or pH adjustment involves additional cost in the way of chemicals employed and procedural steps or operations carried out.

It has also been proposed to use an ammonia, an amine or an alkanolamine salt of polyamine polycarboxylic acid chelating agent in the cleaning of ferrous metals. Solutions of these chelating agents are used at an alkaline pH throughout each of the cleaning and passivating steps and therefore overcome the objection to acidic cleaning solutions. However, such chelating agents tend to be at least moderately expensive.

It is therefore a principal object of the invention to provide a method of cleaning ferrous metal surfaces which employs an alkaline solution throughout the cleaning and passivating steps.

A further object of the invention is to provide a cleaning solution for the cleaning and passivating of ferrous metal surfaces in which the cleaning agent employed is of moderate cost.

These and other objects and advantages of the present invention will be more clearly understood by those skilled in the art upon becoming familiar with the following description and the illustrative examples.

The invention is based on the discovery that a copper bearing deposit is readily removed from a ferrous metal surface and the surface is readily passivated upon contacting the ferrous metal surface with an aqueous alkaline solution having a pH of about 7 to 10 and containing both a nitrogen free polycarboxylic acid complexing agent and a polyamine polycarboxylic acid chelating agent, the aqueous solution being maintained at a temperature in the range of about 200 to 360° F. until the deposit is substantially dissolved.

For the purposes of the specification and the appended claims, the term polyamine polycarboxylic acid chelating agent is understood to refer also to polyamine polycarboxylic acids which are complexing agents.

The complexing agents employed are di-, tri- or polycarboxylic acids containing from 2 to about 8 carbon atoms and having no nitrogen atoms in the molecule. Preferably the complexing agent is a hydroxy polycarboxylic acid. Generally, saturated aliphatic acids are used, though aromatic acids and unsaturated aliphatic acids have also been found suitable. Examples of suitable complexing agents include citric acid, oxalocitraconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and phthalic acid. Of these, citric and tartaric acids are to be preferred.

Suitable polyamide polycarboxylic acid chelating agents for use in the practice of the present invention include the alkylene polyamine polyacetic acids of the formula

$$(HOOCCH_2)_2N[(CH_2)_nN(CH_2COOH)]_mCH_2COOH$$

wherein *n* is an integer from 1 to 4 inclusive and *m* is a numeral in the range of 0 to 4 inclusive and wherein up to two of the carboxymethyl groups may be replaced with a β-hydroxyethyl group and one or more of the carboxymethyl groups may be replaced by carboxyethyl groups. Specific examples of such acids which are particularly suitable are ethylenediaminetetraacetic acid (EDTA), N - hydroxyethyl ethylenediaminetriacetic acid, nitrilotriacetic acid, N - 2 - hydroxyethylminodiacetic acid, diethylenetriaminepentaacetic and mixtures thereof.

These polycarboxylic acid chelating agents are normally employed in the form of the ammonia, amine or alkanolamine salts thereof.

Examples of suitable paired combinations of ammonia, amine or alkanolamine with such polycarboxylic acids are listed in the following table:

Amine:	Polyamine polycarboxylic acid
Ammonia	EDTA.
Ethanolamine	EDTA.
Ethylamine	EDTA.
Ethylenediamine	EDTA.
Diethylenetriamine	EDTA.
Pentaethylenehexamine	EDTA.
Dimethylamine	EDTA.
Trimethylamine	EDTA.
Ethyleneimine	EDTA.
Ethanolamine	Ethylenediaminetetrapropionic acid.
Ethylenediamine	N,N-di(β-hydroxyethyl) glycine.
Ammonia	Tetramethylenediamine-N,N,N′,N′-tetraacetic acid.
Ammonia	(2-hydroxyethylimino) diacetic acid.

Preferably little more than sufficient polyamine polycarboxylic acid chelating agent is used than is required so that its chemistry prevails, especially during the passivation step. The ratio of the moles of nitrogen-free complexing agent used to the moles of polyamine polycarboxylic acid chelating agent should be in the range of about 0.5 to about 50 and preferably about 4 to 20. Generally, the cleaning solution contains from about 1 to 40 percent by weight collectively of nitrogen-free complexing agent and polyamine polycarboxylic acid chelating agent, each being present at least in the amount of 0.5 percent by weight or more.

In carrying out the cleaning of ferrous metal surfaces such as the cleaning of a high pressure boiler an aqueous solution is made up which contains both nitrogen-free complexing agent and polyamine polycarboxylic acid chelating agent in predetermined amounts and ratios within the range set forth hereinabove. A frequently used total amount is in the range of about 4 to about 20 percent by weight and a desirable weight ratio is from 5 to about 10 parts of nitrogen-free complexing agent per part of polyamine polycarboxylic acid chelating agent. The solution is brought to a pH in the range of 7 to about 11 and more preferably 7.5 to about 9.6, by the addition of ammonia, an amine or an alkanolamine. The order of addition of materials to the water employed to make up the solution is not critical.

The solution is brought into contact with the ferrous metal surface at a sufficient temperature to accomplish cleaning in a reasonable period of time such as 1 to 8 hours or more. Temperatures may be in the range of 200 to 360° F. Usually a temperature of about 220° F. suffices. Such temperatures may not be attained in an open system and thus a closed vessel such as a boiler will reach an autogenous pressure corresponding to the temperature employed.

After sufficient time for removal of deposits from the ferrous metal, the pH of the cleaning solution is re-adjusted, if necessary, to bring the pH to a value in the range of 7 to 11. Adjustment is made as before by the addition of ammonia, an amine or an alkanolamine. The temperature of the solution is reduced to about 100 to 180° F. and more preferably about 140 to 160° F. Passivation is then carried out by the addition of an oxidizing agent such as nitric acid, sodium nitrite, ammonium persulfate, ammonium bromate, potassium dichromate, alkali metal or alkaline earth metal molybdates, the readily soluble tungstates, ferric salts such as ferric citrate or ferric nitrate, or, an ammonia, amine or alkanolamine salt of a ferric chelate of a polyamine polycarboxylic acid chelating agent. The foregoing are generally added in the form of concentrated aqueous solutions, except for the chelating agent which is generally provided in situ. The simplest oxidizing agent to add is air.

Addition of oxidizing agent preferably continues, as described in copending application Ser. No. 504,983, filed Oct. 24, 1965, now U.S. Patent 3,413,160, until the oxidation potential of the solution is in the range of about 250 to 175 millivolts as measured with a ferrous metal electrode with reference to a saturated calomel electrode. When a platinum electrode is used instead of a ferrous metal electrode, the equivalent range is about 240 to 165 millivolts. The ferrous metal surface is then in a passivated condition and addition of oxidizing agent must be stopped. The cleaning solution is drained away and the ferrous metal is rinsed with clean neutral water. The cleaned surfaces are found to be copper free and passive, i.e., free of rust spots. In many instances, when using the improved method of the invention, the passivity of the freshly cleaned surface appears to remain for several days.

The present method and composition are especially applicable to the cleaning of mild steel having deposits thereon of iron oxides containing copper or copper oxide with or without hardness deposits and with or without nickel oxide present.

The following examples serve to illustrate the invention and do not limit the scope thereof.

EXAMPLE 1

Comparison run

In a control test run for purposes of comparison, 5 liters of aqueous solution containing 100 grams of citric acid and adjusted to a pH of 9 by the addition of ammonia were placed in boiler tubes having mill scale deposits on the inner surfaces thereof. The boiler tubes were interconnected as part of a closed system. Two grams of copper oxide were added to the solution to similate actual boiler conditions and the system was heated to 220° F. and under autogenous pressure for 20 minutes. The temperature was then reduced to 212° F. and the system was let stand for 2 hours. During the second hour, iron powder was added so that the citric acid would spend excess complexing power upon the iron powder.

The system was then opened and the tubes were examined visually and found to have some loose black deposits on the inner surfaces thereof although the tubes were generally clean. The solution was found to contain 0.28 percent by weight iron or a sufficient amount to use 48 percent of the binding power of the citric acid present.

The pH was re-adjusted to 9 with ammonia and the temperature was reduced to 170° F. Air was then bubbled through the solution at a rate of 0.5 cubic feet per minute (c.f.m.) for 39 minutes. The potential of the solution as measured by a platinum electrode versus a saturated calomel electrode was 356 millivolts. The boiler tubes were drained, filled with fresh water and drained again. Visual inspection of the boiler tubes showed that quantities of copper were visible on the inside surfaces and after rusting had already occurred.

Run according to the invention

Four grams of ethylenediaminetetraacetic acid and 2 grams of copper oxide were added to the citric acid solution drained from the boiler tubes in the comparison run. The solution pH was adjusted to a value of 9 and the solution was placed in mill scaled boiler tubes as before and heated to 220° F. under autogenous pressure for 20 minutes. The temperature was then reduced to 212° F. and the tubes were allowed to stand for 2 hours before a sample of the solution was taken. Chemical analysis of the sample showed that it contained 0.59 percent by weight of iron which corresponds to 98 percent of the binding power of the citric acid present. The solution temperature was reduced to 170° F., the pH was adjusted to 9 with ammonia and air was bubbled through the solution at the rate of 0.5 c.f.m. The solution did not turn dark yellow black, the color of iron citrate, but instead it turned brownish. After 25 minutes of adding air, the potential of the solution was 185 millivolts as measured by a platinum electrode with reference to a saturated calomel electrode. The addition of air was stopped, the tubes were drained, filled with fresh water and drained again. Visual examination of the tubes showed that they were clean, copper-free and passive. Repeated inspection showed that the passivity persisted for several days.

EXAMPLE 2

Six grams of ethylenediaminetetraacetic acid and 100 grams of citric acid were dissolved in about 5 liters of water and the pH of the resulting solution was adjusted to 9 with ammonia. Two grams of copper oxide were added to the solution and the solution was placed in mill scaled boiler tubes. The boiler tubes were heated under autogenous pressure to 220° F. for 20 minutes. The temperature was then reduced to and held at 212° F. for 2 hours. During the second hour iron powder was added to the solution so that the acids became spent thereon. The tubes were then examined and found to appear extremely clean. The solution was analyzed and found to contain 0.63 percent iron or somewhat more than the citric acid alone could complex. The pH was re-adjusted to 9, the temperature was lowered to 170° F., and air was introduced for a period of 22 minutes at a rate of 0.5 c.f.m. At this point the solution potential was 200 millivolts as measured by a platinum electrode versus a saturated calomel electrode. The tubes were drained, filled with fresh water and drained again. Inspection of the tube surfaces showed that they were clean, copper-free, passive and bright.

EXAMPLE 3

The proceduce described in the foregoing examples was repeated using 5 liters of a solution containing 1.1 percent by weight of ethylenediaminetetraacetic acid and 0.5 percent by weight citric acid and having the pH adjusted to 9 with ammonia. At the completion of the cleaning step the solution was found to contain 0.56 percent iron, i.e., it was aproximately completely spent. Upon carrying out an air blowing step approximately as described above and draining and rinsing the tubes, the tubes were found to be clean and passive.

Comparison run

An additional control test was carried out by way of comparison. Five liters of a solution containing 2 percent by weight of citric acid and no ethylenediaminetetraacetic acid or ammonia was used to clean mill scaled boiler tubes in a manner similar to that described in the foregoing examples. At the completion of the cleaning step, the iron content of the solution was 0.28 percent showing that the citric acid was not efficiently used. The cleaning rate was very slow and it appeared that a higher temperature would be necessary to complete the cleaning step.

Among the advantages of the invention is the ease (1) of achieving effective cleaning and (2) of obtaining good passivation of the ferrous metal surfaces at the conclusion of the cleaning operation, the results being superior to cleaning with either of citric acid or ethylenediaminetetraacetic acid alone.

The method and composition of the invention having been thus fully described, various modifications thereof will at once be apparent to those skilled in the art and the scope of the invention is to be considered limited only by the breadth of the claims hereafter appended.

I claim:

1. The method of removing a copper bearing deposit from a ferrous metal surface which comprises:

contacting the ferrous metal surface with an aqueous alkaline solution having a pH of about 7 to 11 and containing both a nitrogen-free polycarboxylic acid complexing agent and an ammonia, amine or alkanolamine salt of polyamine polycarboxylic acid chelating agent, the aqueous solution being maintained at a temperature in the range of about 200 to 360° F. until the deposit is substantially dissolved.

2. The method as in claim **1** in which the solution contains at least 0.5 percent by weight of each of the nitrogen-free complexing and polyamine polycarboxylic acid chelating agent and up to 40 percent by weight collectively of both.

3. The method as in claim **1** in which the nitrogen-free complexing agent is citric acid.

4. The method as in claim **1** in which the temperature of the aqueous solution is lowered, if necessary, to bring the solution to a temperature in the range of about 100 to 180° F., and an oxidizing agent is added to the solution until the oxidation potential of the solution, as shown by a ferrous metal electrode in the solution with reference to a standard calomel electrode, falls to a value in the range of about 175 to 250 millivolts.

5. The method as in claim **4** in which the nitrogen-free complexing agent and the polyamine polycarboxylic acid chelating agent have bound thereto from 60 to 97 percent of their collective iron binding capacity.

6. The method as in claim **1** in which the ratio of the number of moles of nitrogen-free complexing agent to the number of moles of polyamine polycarboxylic acid chelating agent employed is a number in the range of 0.5 to about 50.

7. The method as in claim **6** in which the said ratio is a number in the range of about 4 to 20.

8. An aqueous cleaning solution for the cleaning of ferrous metal which comprises:

from about 1 to 40 percent by weight collectively of a nitrigen-free polycarboxylic acid complexing agent, and an ammonia, amine or alkanolamine salt of polyamine polycarboxylic acid chelating agent, the solution cointaining at least 0.5 percent by weight of each of the said complexing agent and the said chelating agent, and the solution having a pH in the range of about 7 to 11.

9. The cleaning solution as in claim **8** wherein the complexing agent is citric acid.

10. The cleaning solution as in claim **8** wherein the polyamine polycarboxylic acid chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, nitriotriacetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid, and mixtures thereof.

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MORRIS O. WOLK, *Primary Examiner.*

SIDNEY MARANTZ, *Assistant Examiner.*

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