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METAL CLEANING SOLUTION OF CHELATING AGENT AND WATER-SOLUBLE SULFIDE

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ABSTRACT OF THE DISCLOSURE

In cleaning a ferrous based metal surface to remove surface deposits therefrom, from about 0.001 to about 0.1 percent by weight of a water-soluble sulfide capable of releasing sulfide ions in aqueous medium is added to the aqueous cleaner comprising aqueous alkaline solution of an alkylene polyamine polyacetic acid chelating agent.

FIELD OF THE INVENTION

The invention relates to an improved method of cleaning metal surfaces with an aqueous alkaline solution of a strong chelating agent and to the improved solution employed in the method. A strong chelating agent is understood to be a chelant which binds dissolved iron tightly in competition with sulfide ion so as to substantially avoid formation of iron sulfide solids.

BACKGROUND OF THE INVENTION

In the construction of boilers it is common practice to install metal tubes without the removal of the mill-scale normally formed on such tubes during their manufacture. In addition, most boiler preheater sections are made of copper or a copper-bearing metal, such as brass or bronze, so that copper is carried into the boiler during operation of the boiler, and forms a deposit which accelerates galvanic corrosion and adversely affects heat exchange through the boiler tubes. When the boiler is cleaned and an attempt is made to remove mill-scale, the copper coating not only interferes with the removal of mill-scale by the cleaning solution, but also, copper plates out on the cleaned surface. If the copper is not subsequently removed, the deposited copper causes accelerated galvanic corrosion, especially when the boiler is placed back in operation.

OBJECTS OF THE INVENTION

A principal object of the invention is to provide an improved method of cleaning a metal surface with an aqueous alkaline solution of a chelating agent.

A further object of the invention is to provide an improved aqueous alkaline cleaning solution to be employed in the present method.

Yet a further object of the invention is to provide an improved method of removing copper deposits and preventing their redeposition when using, as the cleaning solution, an aqueous solution of an alkylene polyamine polyacetic acid chelating agent.

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 appended claims.

STATEMENT OF THE INVENTION

The invention is based on the discovery that upon contacting a ferrous metal surface having mill-scale or hardness deposit thereon with an aqueous alkaline solution of a strong chelating agent containing from about 0.001 to about 0.1 percent by weight of a water soluble sulfide capable of providing sulfide ions, the cleaning action of the cleaning solution is not only speeded up, but copper, if present in the solution, is prevented from depositing on the ferrous metal. Preferably the concentration of soluble sulfide is at least 0.005 percent by weight.

BRIEF DESCRIPTION OF THE INVENTION

The present solution and the cleaning method are especially applicable to the cleaning of ferrous metal surfaces including the stainless steels as well as mild steel and cast iron.

Any water soluble sulfide may be used providing (1) a high proportion of the sulfide molecules, e.g., at least 50 percent, and preferably at least 80 percent, are capable of releasing sulfide ions in the solution, (2) the cation involved, e.g., a metal cation, does not plate out on the cleaned ferrous metal surface or form an undesirable complex with the chelating agent, (3) the sulfide is not too toxic for safe handling, and (4) the sulfide has a water solubility of at least about 0.1 percent by weight. Accordingly, either an inorganic sulfide or an organic sulfide with the requisite characteristics may be used. Examples of inorganic sulfides usable according to the invention are sodium sulfide, potassium sulfide and ammonium sulfide. Examples of suitable organic sulfides are thioglycolic acid, mercaptobenzothiazole and dithioethanol. Suitable organic sulfides need not ionize but they must at least dissociate in a manner to effectively free the sulfur atoms therein for reaction with soluble copper, and such behavior is to be considered, for the purposes of the description and the claims herein, as embraced by the term, releasing sulfide ions. Economics generally dictate that potassium sulfide or sodium sulfide will be used.

The cleaning solutions which are improved by the addition of soluble sulfide ion are those containing an alkylene polyamine polyacetic acid chelating agent, in a concentration range of about 0.5 to 40 percent and more generally about 5 to about 20 percent by weight. The suitable polyacetic acids are embraced by 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 ethylenediamintetraacetic acid (EDTA), N-hydroxyethyl ethylenediaminetriacetic acid, nitrilotriacetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid and mixtures thereof.

These polyacetic 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 polyacetic acids are listed in the following table.

Amine:	Polyacetic 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.

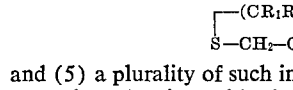
Cleaning of metal surfaces with the improved solution may be carried out at temperatures up to the stability limit of the chelating agent in aqueous solution. More generally, cleaning is carried out at a temperature in the range of 70 to 190° C. While the pH is not sharply critical for the purposes of the invention, it is preferred to use the solutions of alkylene polyamine polyacetic acids at a pH in the range of about 7 to about 11 and more preferably at a pH in the range of about 8 to 10.

Although it has generally been considered helpful to pressurize the system when cleaning with an aqueous alkaline solution of chelating agent containing no additive, the application of pressure is not necessary, though not adverse, when using the present improved solution containing soluble sulfide.

If desired, any of various available inhibitors may be employed to minimize the attack of the chelating agent upon the ferrous metal substrate. Examples of suitable inhibitors are found in the group consisting of: (1) $A—S_x—(CH_2)_n—NHR_1$, wherein x is 1 or 2, n is an integer in the range of 1 to 8 inclusive, R_1 is lower alkyl, and A is hydrogen, lower alkyl, or $R_2—NH—(CH_2)_m—$ wherein R_2 is lower alkyl and m is an integer in the range of 1 to 8 inclusive; (2) hydrosulfide salt of said $A—S_x—(CH_2)_n—NHR_1$; (3)



wherein R_1, R_2, and R_3 are each hydrogen or lower alkyl and n is 1, 2 or 3; (4) hydrosulfide salt of said



and (5) a plurality of such inhibitors in combination.

During cleaning with the present improved solution, copper deposits present on the ferrous metal surface are dissolved by ferric ions entering the solution. The dissolved copper is converted by the sulfide into a very fine precipitate of copper sulfide. This precipitate may adhere lightly to the cleaned metal surface but it is easily flushed from the surface by a turbulent flow of water. The sulfide may be added at most any stage of the cleaning to prevent redeposition of copper. However, to get the full benefit of the sulfide addition, in the form of more rapid initial cleaning, it is highly desirable to add the sulfide when the cleaning operation begins.

Because there is some tendency for ferrous metal surfaces cleaned in this manner to exhibit a propensity for rusting quickly at the termination of the cleaning operation, it is generally desired to use more than about 0.01 percent of soluble sulfide. Generally, use of about 0.05 percent of soluble sulfide results in a clean passivated ferrous metal surface at the termination of the cleaning operation.

The theory of the invention is not completely understood, but it is believed that additions of sulfide according to the invention bring about precipitation of Cu_2S, not only resulting in favorable stoichiometry, but also substantially preventing disproportionation of cuprous ion to cupric ion and copper metal. It is apparently the copper metal which precipitates on freshly cleaned ferrous metal surfaces.

EXAMPLES

The following examples are presented by way of illustration and do not limit the scope of the invention.

Example 1

300 milliliters of an aqueous alkaline solution containing 6.6 percent by weight of ethylenediaminetetraacetic acid was added to each of two beakers. To the second beaker there was also added 0.03 gram of potassium sulfide according to the invention. The contents of each beaker were brought to and maintained at a temperature of 90° C. Three 1010 steel coupons (AISI) were placed in each beaker.

In each case one of the coupons had been treated so as to develop a surface entirely covered with mill-scale. A second coupon having a similar covering of mill-scale was also provided over half of its surface with a plating of copper. In each case the third coupon was prepared by pickling to provide a clean surface after which copper was plated directly on the steel throughout half of the surface. Within 25 minutes, on using the method and composition of the invention, the coupon covered with mill-scale and the coupon having both mill-scale and a partial coating of copper were each cleaned and the cleaned coupon having a partial coating of copper was covered with a thin film of copper sulfide which could easily be rubbed off. After a thorough rinsing with clear water these coupons were all clean and bright but they rusted quickly indicating a need for a passivation step following cleaning as well understood in the art.

In the comparison test in which the coupons were exposed to the cleaning solution which did not contain sulfide the coupons were not cleared of mill-scale until 115 minutes had elapsed. It was then found that all the coupons were evenly plated with the copper which had been dissolved in the cleaning process.

On repeating the foregoing experiment but using 0.05 percent instead of 0.01 percent by weight of potassium sulfide mill-scale was removed from the coupons in 25 minutes, the copper did not plate out on the cleaned metal and the coupons on being rinsed were passive and did not rust.

Example 2

In an additional series of tests, solutions of various chelating agents and water soluble sulfides are employed, respectively, in cleaning three substantially identical high pressure steam boilers to remove hardness and iron oxide deposits commingled with copper deposits. Each boiler is filled with sufficient aqueous cleaning solution of pH 8.3 to circulate well and reach all critical surfaces, or about 10,000 gallons of solution. Each solution contains about 15 percent by weight of alkylene polyamine polyacetic acid chelating agent and 0.05 percent by weight of a water soluble sulfide capable of providing sulfide ions for tying up copper ions.

The chelating agent in the first boiler is ethylenediaminetetraacetic acid and the soluble sulfide is sodium sulfide.

The chelating agent in the second boiler is N-hydroxyethyl ethylenediaminetriacetic acid and the soluble sulfide is ammonia sulfide.

The chelating agent in the third boiler is diethylenetriaminepentaacetic acid and the soluble sulfide is thioglycolic acid.

The cleaning solution in each boiler is brought to a temperature of 140° C. and maintained at about that temperature while being circulated through the boiler system. After about 20 hours substantially all hardness and iron oxide deposits and dissolved and copper present in the deposits is dissolved and carried as a finely divided copper sulfide precipitate in the solution or lightly deposited precipitate on the cleaned ferrous metal surfaces. The copper sulfide precipitate is mainly Cu_2S.

The solution in each boiler is drained off and each boiler is water rinsed several times with about 11,000 gallons of water per rinse. Each boiler is then opened and inspected. The ferrous metals are found to be clean and gun metal blue in appearance.

In a manner similar to that set forth for the foregoing examples, cleaning solutions can be prepared using any of the polyacetic acid chelating agents and water soluble sulfides disclosed herein in various combinations within the concentration ranges set forth and these used in accordance with the present novel process.

The method and improved solution of the invention having been thus 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. In a process of cleaning a ferrous based metal surface to remove surface deposits therefrom by contacting said surface with an aqueous alkaline solution of an alkylene polyamine polyacetic acid chelating agent, the improvement which comprises: contacting said metal surface with an aqueous alkaline solution of alkylene polyamine polyacetic acid having dissolved therein from about 0.001 to about 0.1 percent by weight of a water soluble sulfide, the sulfide being further characterized as (1) having a high proportion of molecules capable of releasing sulfide ions, (2) having substantially no cations which will plate out on the clean ferrous based metal surface, (3) being relatively safe to handle, and (4) having a water solubility of at least about 0.1 percent by weight in the cleaning solution.

2. The process as in claim **1** in which the sulfide is selected from the group consisting of sodium sulfide, potassium sulfide and ammonium sulfide.

3. The process as in claim **1** in which the sulfide is selected from the group consisting of thioglycolic acid and dithioethanol.

4. The process as in claim **1** in which the sulfide is sodium sulfide.

5. The process as in claim **1** in which the concentration of the sulfide is about 0.05 to about 0.1 percent by weight.

6. The process as in claim **1** in which the cleaning is carried out with the said solution at a temperature in the range of about 70 to 190° C.

7. The process as in claim **1** in which the alkylene polyamine polyacetic acid is ethylenediaminetetraacetic acid.

8. The process as in claim **1** in which the surface deposits contain copper or copper compounds.

9. A metal cleaning solution as employed in the process of claim **1** which comprises: from about 0.001 to about 0.1 percent by weight of said water soluble sulfide, from about 0.5 to about 40 percent by weight of alkylene polyamine polyacetic acid, sufficient ammonia or caustic to bring the solution to a pH in the range of about 7 to about 11, and the balance substantially water.

10. The composition as in claim **9** which contains from about 0.05 to about 0.1 percent by weight of said water soluble sulfide.

11. The composition as in claim **9** in which the sulfide is sodium sulfide and the alkylene polyamine polyacetic acid is ethylenediaminetetraacetic acid.

12. The composition as in claim **9** which contains, in addition, an inhibitor, said inhibitor being characterized as beng capable of minimizing the attack of the alkylene polyamine polyacetic acid on the ferrous based metal substrate.

References Cited

UNITED STATES PATENTS

3,447,965 6/1969 Teumac ---------- 252—82 X

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