ABSTRACT: The invention is based on the discovery that upon adding a polycrylamine having intralinear amino groups to an aqueous alkaline solution of an ammoniated or aminated polycarboxylic acid chelating agent, a new and improved metal-cleaning solution is provided. Upon bringing such cleaning solution into contact with a ferrous metal surface having hardness and/or iron oxide scale, and copper, thereon and the solution being maintained at a temperature above about 155°C for a time sufficient to dissolve all the hardness and iron oxides, the copper is dissolved and neither precipitates from solution nor deposits on the ferrous metal surface.
CLEANING OF FERROUS METAL SURFACES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to an improvement in the method of cleaning ferrous metal surfaces, such as steam boilers having copper components in the system, with an aqueous alkaline solution of polycarboxylic acid chelating agent and to the aqueous cleaning composition employed in the improved process.

2. Description of the Prior Art

A process for cleaning ferrous metal surfaces has been used in which iron oxides are first removed in an initial cleaning step using an aqueous acidic solution of polycarboxylic acid, after which the solution is made alkaline and a copper removal step is effected. However, it is generally considered better practice to avoid using acidic solutions for the cleaning of boiler systems. Further, two-step methods are not as economical, generally, as one-step methods.

In another process disclosed in a copending patent application, the cleaning solutions consist of an ammoniated or aminated polycarboxylic acid chelating agent and cleaning is carried out under alkaline conditions. This method is effective for the removal of mill-scale and hardness deposits, but is not very effective for the removal of mill-scale having copper deposits therein. Several of the polyaminocarboxylic chelating agents in an attempt to make the solutions suitable for working with copper deposits. For example, a reagent may be added to the cleaning solution which will form a precipitate with the copper removed in cleaning and prevent its deposition on freshly cleaned ferrous metal surfaces. Such a process suffers from the disadvantage that care must be taken to dislodge and remove all of the copper precipitate, usually by a rinse involving a considerable volume of water.

It has also been suggested to add an oxidizing agent to the cleaning solution subsequent to removal of the mill-scale in order to dissolve the copper plated on the clean substrate. This method also suffers from the disadvantage that it is a two-step process.

Objects of the Invention

A principal object of the present invention is to provide an improvement in the method of cleaning a ferrous metal surface, having iron oxides and copper deposited thereon, using an ammoniated or aminated polycarboxylic acid chelating agent, the improvement providing for removal of iron oxides and copper in one operation while avoiding deposition of copper on the freshly cleaned metal substrate.

A further object of the invention is to provide the novel cleaning solutions used in the improved method of the invention.

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

Summary of the Invention

The invention is based on the discovery that upon adding a polyaniline having intralinear amino groups to an aqueous alkaline solution of an ammoniated or aminated polycarboxylic acid chelating agent, a new and improved metal-cleaning solution is provided. Upon bringing such cleaning solution into contact with a ferrous metal surface having hardness and/or iron oxide scale, and copper, thereon and the solution being maintained at a temperature above about 155° C. for a time sufficient to dissolve all the hardness and iron oxides, the copper is dissolved and neither precipitates from solution nor deposits on the ferrous metal surface.

BRIEF DESCRIPTION OF THE METHOD AND COMPOSITION OF THE INVENTION

Any ferrous metal surface may be cleaned using the solution and method of the invention. Examples of such ferrous metals are cast iron, mild steel, and austenitic stainless steel.

Any of the combinations of polycarboxylic acids and amines or amines considered together may be used in a concentration in the range of about 1 to 10 percent by weight.

The polyanilines which may be used are principally the polylkylene polyanilines having intralinear amino groups having a ratio of nitrogen atoms to carbon atoms in the chain of at least about 0.2 and preferably at least about 0.5. In addition, suitable polyanilines must be readily solubilized in the aqueous cleaning solution at an alkaline pH in the range of pH 7 to 10. Specific examples of suitable polyanilines are polyethyleneimine having molecular weights in the range of about 600 to 500,000, the reaction product of ethylenediamine and ethylenedichloride having an average molecular weight above about 230, preferably about 600 to 500,000, polymerized N-phenyl ethylenimine having a phenyl group on about 10 per cent of the ethylene units in the molecule, and pentaethylenemamine. The polyanilines are employed in a concentration range of about 0.2 to 5 percent by weight. In any event, a sufficient amount of the polyaniline must be used to provide two nitrogen atoms for each copper ion which is to be complexed. The amount of polyethyleneimine to meet this requirement is about 2.8 parts per part by weight of copper.

Preferably, the corrosive attack of the polycarboxylic acid chelating agent upon the metal substrate is inhibited by an inhibitor compound or composition that does not interfere with the action of the present polyanilines in keeping copper from plating out on the substrate. Examples of suitable inhibitors include, e.g., sodium mercaptobenzothiazole, di-aminoethylysulphonic acid, or the product of the reaction of (1) one mole of an ammonia derivative having at least one hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen, (2) from 1.5 to 10 moles of a ketone having at least one hydrogen atom on the carbon atom adjacent to the carbonyl group, (3) from 2 to 10 moles of an
aldehyde selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and (4) from 0.6 to 24 parts by weight based on (1), (2), and (3) of a fatty acid having from 1 to 20 carbon atoms at a temperature of from 150° F. to about 250° F. for from 1 to 16 hours, such reaction product being more fully described in U.S. Pat. No. 3,077,454, which is expressly incorporated herein by reference, or mixtures thereof.

In carrying out the improved process as on a boiler system, the system is drained and then refilled with an aqueous solution of the polycarboxylic acid chelating agent having the polyamine dissolved therein. The aqueous solution is heated up in order to dissolve iron oxide or hardness deposits at practical rates. The solution is also heated in order to activate the polyamine. For the latter purpose, temperatures above about 155° C. are employed. Suitable temperatures are in the range of 155° to 190° C. Normally the system is closed and the cleaning solution builds up some autogenous pressure due to the water and the ammonia or other volatile amine present. Pressure of the order of 20 to 200 pounds per square inch gauge are typical, but have no particular effect on the present method. The temperature of the cleaning solution is maintained at least 30 to 60 minutes, or until the iron oxides and other deposits are removed. The process seldom takes more than 4 hours. At the end of this time the cleaning solution is drained and rinsed leaving a clean ferrous metal surface free of copper deposits.

In another embodiment of the present method the polyamine is activated by heating an aqueous solution thereof prior to adding the polyamine to the aqueous alkaline cleaning solution containing the polycarboxylic acid chelating agent. Heating about 10 percent by weight aqueous solution of the polyamine to a temperature at least 155° C. and preferably 160° to 190° C. for 30 minutes provides sufficient pyrolytic activation of the polyamine. With such prior activation outside the system to be cleaned, the cleaning of the ferrous metal surface may proceed at a much lower temperature, usually in the range of 110° to 150° C. The advantage of using such lower temperature is decreased corrosion of the ferrous metal surfaces by the cleaning solution, without in any way interfering with the removal of copper deposits.

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

Example 1
An aqueous solution was prepared containing 3.8 percent by weight of triaminommonium (ethylenedinitrilato) tetraacetate (ammoniated EDTA), 0.3 percent by weight of polyethyleneimine having a molecular weight of about 40,000 to 60,000, 0.5 percent by weight of sodium mercapto- benzothiazole and 0.1 percent by weight of a commercial inhibitor of the class described in U.S. Pat. No. 3,077,454 and consisting of the product of reaction of Rosin Amine D, tall oil fatty acids, acetylphenoxy, and paraformaldehyde at a temperature of about 95° C. for about 8 hours in ethylene glycol medium and in the presence of H₂SO₄. After the reaction, an adduct of nonylphenol and ethylene oxide was added to the reaction product all as more fully described in said U.S. Pat.

A 200 millilitre quantity of this solution was placed in a glass beaker along with two 1010 (AISI) steel coupons having a natural mill-scale surface thereon. 0.3 grams of copper powder admixed with 0.7 grams of ferric oxide powder were also placed in the same glass beaker. The beaker and contents were placed in a pressure vessel. The vessel was closed and heated to 187° C. The autogenous pressure in the vessel rose to 180 pounds per square inch gauge. After 4 hours at the stated temperature the reaction was quenched with water and opened. The beaker and contents were removed. The coupons were found to be bright and clear and free of copper deposits.

Comparison Test
In an experiment made by way of comparison, a run was carried out as described in Example 1 except that the polyethyleneimine was omitted from the aqueous cleaning solution. When the coupons were removed from the pressure vessel they were found to be free of mill-scale but heavily coated with copper.

Example 2
On carrying out a run in the same manner as Example 1 except that a polyethyleneimine having 10 percent phenyl substitution in the molecule was substituted weight by weight for the polyethyleneimine of Example 1, the mill-scale coated coupons were cleaned and copper did not deposit on the cleaned surfaces.

Example 3
On carrying out a run in the same manner as Example 1 except for the substitution of a linear polyalkylene polyaniline for polyethyleneimine the mill-scale coupons came out bright and clean and free of copper deposits. The linear polyalkylene polyaniline used was a reaction product of ethylenediamine and ethylene dichloride and was estimated to have an average molecular weight greater than 600.

Comparison Test
In a run made by way of comparison, all conditions and reactants were the same as in Example 1 except that the pressure vessel and contents were heated only to 115° C. The coupons were cleaned of mill-scale but carried heavy copper deposits.

Example 4
A solution containing 3.8 percent by weight of triaminommonium (ethylenedinitrilato) tetraacetate, and 0.25 percent of approximately 50,000 was prepared and 200 milliliters of this solution was placed in a glass beaker along with two 1010 (AISI) steel coupons which had been cleaned in nitric acid, dried and weighed. The beaker and contents were placed in a pressure vessel and heated to 150° C. The temperature was maintained for 4 hours after which the pressure vessel was quenched and opened. The coupons were dried and weighed and corrosion of the metal was found to have taken place at the rate of 0.0605 pounds per square foot per day (lb/ft²/day).

Example 5
When the test as in Example 4 was conducted using magnetite coated coupons instead of acid cleaning coupons the corrosion rate was found to be 0.0326 lb/ft²/day.

Example 6
A run was carried out in the same manner as Example 5 except that sodium mercaptobenzothiazole and the commercial inhibitor described in Example 1 were added to the last solution in the same proportions as in Example 1. The coupons subject to test corroded at a rate of 0.0043 lb/ft²/day.

Example 7
A solution containing 3.8 percent by weight of triaminommonium (ethylenedinitrilato) tetraacetate and 0.3 percent by weight polyethyleneimine and 0.15 percent by weight copper oxide was prepared and 200 milliliters of this solution was placed in a glass beaker. The beaker was placed in a pressure vessel and the vessel and contents were heated to 160° C. for about 30 minutes. The pressure vessel was then cooled and opened and two 1010 (AISI) steel coupons having a surface covered with mill-scale were placed in the beaker. The pressure vessel was then closed and heated to 115° C. The temperature was maintained for 4 hours, after which the pressure vessel was cooled and opened and the coupons examined. The coupons were found to be free of copper plating and they showed corrosion had taken place at the rate of 0.0173 lb/ft²/day.

Comparison Test
On carrying out a run in about the same manner as Example 7 except that the inhibitors of Example 1 were added to the cleaning solution, initial heating was carried out at 165° C. and
the preheated cleaning solution was transferred anaerobically to another pressure vessel containing the two mill-scaled coupons, and the second pressure vessel was heated only to 97°F during the 4 hour period. The coupons under test were cleaned of mill-scale and showed that corrosion had taken place at a rate of 0.0091 lb./ft²/day, but copper had plated out on the coupons.

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.

We claim:

1. An aqueous composition for the removal of scale from ferrous metals and the prevention of the deposition of copper on freshly cleaned ferrous metal surfaces which consists essentially of:
   A. 1–10 percent by weight of a polyacetic acid chelating agent selected from the group consisting of: ethylenediaminetetraacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, nitrilotriacetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriamine-pentaacetic acid, and mixtures thereof.
   B. 0.1–5 percent by weight of a polyalkylenepolyamine selected from the group consisting of polyethylenimine having a molecular weight of about 40,000 to 60,000 and polyethylenimine having a molecular weight of about 40,000 to 60,000 which contains 10 percent N-phenyl substitution;
   C. Sufficient ammonia or amine to bring the solution pH to about 7–10; and
   D. water.

2. The composition as in claim 1 which contains a corrosion inhibitor selected from the group consisting of sodium mercaptobenzothiazole, di-aminoethyl sulfide, the product of reaction of (1) 1 mole of an ammonia derivative having at least one hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen, (2) from 1.5 to 10 moles of a ketone having at least one hydrogen atom on the carbon atom adjacent to the carbonyl group, (3) from 2 to 10 moles of an aldehyde selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and (4) from 0.6 to 24 parts by weight based on (1), (2), and (3) of a fatty acid having from 1 to 20 carbon atoms, at a temperature of from about 150°F to about 250°F. for from 1 to 16 hours, and mixtures thereof.
UNIVERS STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,627,687 Dated December 14, 1971

Inventor(s) Fred N. Teumac and James S. Scruggs

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 3, in the formula, change "D" to -- C --.
Column 2, line 49, after "suitable" delete "polyethylenimine"
and insert -- polyamines --.
Column 3, line 12, after "aqueous" insert -- alkaline --.
Column 4, line 35, after "percent" insert -- by weight of a
polyethylenimine having a molecular weight --.
Column 4, line 58, after "percent" insert -- by weight --.

Signed and sealed this 25th day of July 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. ROBERT GOTTSCHALK
Attesting Officer Commissioner of Patents