PROCESS FOR REMOVING COPPER-CONTAINING IRON OXIDE SCALE FROM METAL SURFACES

Salvatore Alfano, Houston, Tex., assignor to Chas. Pfizer & Co., Inc., Brooklyn, N.Y., a corporation of Delaware
No Drawing. Filed Feb. 14, 1961, Ser. No. 89,116
9 Claims. (Cl. 134—3)

This invention is concerned with the cleaning of metal surfaces and more particularly with a new and valuable process for the removal of iron oxide scale from metals.

Operational scale deposited in steam-generating equipment usually consists of oxides of iron, often magnetite (Fe₃O₄), iron oxide (Fe₂O₃), and iron hydroxide (Fe(OH)₃). Where the unit is fabricated in part from alloys of copper, e.g., for the condensers, the scale will be found to contain copper as well, in the form of the elemental metal and sometimes as cuprous and cupric oxides. Such scale is generally tightly adherent and low in porosity. Its gradual build-up reduces heat transfer and water circulation to the point where, usually every one to four years, it must be removed. Since the shutdown of a high capacity boiler can easily represent losses of thousands of dollars per day, it is obvious that the most rapid and effective cleaning is desirable.

In the past, hydrochloric and other mineral acids have been employed for this purpose. However, it has been found that where the scale contains copper or copper oxides, iron oxide scale removal is accompanied by redeposition or plating out of elemental copper throughout the system. This copper not only accelerates corrosion and interferes with the exchange, but it may flake off during operation and be carried through the superheater, causing expensive damage to the turbine surfaces.

Furthermore, high pressure boilers containing austenitic parts, e.g., superheater tubes, and operating at pressures of 2500-3000 p.s.i. and higher are subject to chlorides stress fatigue, and these hydrochloric acid is frequently unsuitable as a cleaning agent. Mineral acids in general have the added disadvantage of attacking steel, even where corrosion inhibitors are incorporated, and present a safety hazard to personnel. Because of these problems, the non-toxic acids such as citric have been tested. Citric acid offers advantages in cleaning and its scale formation is not substantial, which scale becomes a part of the safety to equipment and personnel, and because it readily dissolves rust and mill scale. However, dense operational scales containing magnetite are removed quite slowly by citric acid, and where copper is present the objectionable copper plating is encountered.

Since no satisfactory cleaning solution has been available to overcome all of these difficulties, the use of a series of solutions has been proposed to remove the various components of operational scale and to provide a relatively clean surface resistant to rapid re-corrosion. Such processes are only partially successful and, since they entail many time-consuming rinsing steps, may require 24 hours or more to complete. They therefore involve high costs in lost operation, and also usually require appreciable quantities of expensive ingredients. Additionally, where such processes employ a hydrochloric acid step they retain many of the described disadvantages and are usually not applicable to the cleaning of high pressure boilers containing austenitic materials.

Accordingly, it is an object of the present invention to provide a process for the rapid and complete removal of copper-containing iron oxide scales from metal surfaces.

Another object is to provide such a process which will remove both copper and iron oxide deposits in a single solution, without the necessity for intermediate drainage and rinsing.

Another object is a process which is safe to both personnel and equipment, and which may be used even with very high pressure units containing austenitic alloys.

Another object is a process which is rapidly effective even where tightly adherent magnetite scale predominates.

Still another object is a cleaning process which efficiently utilizes relatively low concentrations of inexpensive, readily available cleaning ingredients.

These and other objects are achieved by the new process of the present invention, which comprises an acidic iron-oxide-removing step followed by an alkaline copper-complexing step, both carried out in a single solution.

Acidic step.—The first step of the new process consists of contacting the scaled surfaces with an aqueous solution of citric acid adjusted to a pH between about 2.5 and about 5 with a nitrogen base. While other acids, such as gluconic, tartaric, oxalic, lactate, glucouronic, glycollic, saccharic or maleic acids, or mixtures thereof, may be effective in varying degree in the first step of my new process, citric acid possesses the virtues of high effectiveness, low corrosion rate, non-toxicity, ready availability and low cost. Mineral acids are not suitable.

The nitrogen base which I employ for the pH adjustment may be ammonia, an ethanolamine, or an aliphatic hydrocarbon amine. By "ethanolamine" I mean ethanolamine, diethanolamine or triethanolamine. Any aliphatic hydrocarbon amine, secondary or tertiary, may be employed, provided that it is water-soluble. Such amines include trimethylamine, diethylamine, the various primary butyl- and aminolines, ethylenediamine, propylamine, dimethylamine, triethylenediamine, and the like. Ordinarily, ammonia will be preferred for its low cost and high effectiveness.

For high capacity and rapid cleaning I employ the citric acid in a concentration of at least about 1% w./v. Any concentration above 1% up to saturation may be used, but ordinarily concentrations above 10% w./v. offer no added advantage and are unnecessary. Concentrations between about 1.5 and about 3% w./v. are generally preferred. The expression "w./v." means grams per 100 milliliters; of page xi, Merck Index, 6th edition, 1952.

As previously stated, I adjust my citric acid solution to a pH between about 2.5 and about 5 with the base. Alternatively, I may dissolve monoammonium citrate in water to provide a solution of equivalent concentration. Such a solution has a pH of about 3.5-4. Solutions having a pH appreciably above 5 react only very slowly with magnetite scale and are therefore not preferred. It is particularly surprising, however, that citrate solutions having a pH appreciably below 2.5 are also quite slow in dissolving operational magnetic scale. The following table presents a comparison of the degree of effectiveness of various citrate solutions under equivalent conditions of time and temperature, as observed in a laboratory test with a magnetite scale.

<table>
<thead>
<tr>
<th>Solution:</th>
<th>Percent scale removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% citric acid</td>
<td>25-30</td>
</tr>
<tr>
<td>10% citric acid</td>
<td>40-45</td>
</tr>
<tr>
<td>3% citric acid + NH₄⁺ to pH 3</td>
<td>98-99</td>
</tr>
</tbody>
</table>

This surprising effect is especially advantageous since the corrosion rate of bare metal by citrate at the optimum pH values is so low that corrosion inhibitors are normally unnecessary.

In cleaning steam generating equipment, to insure adequate contact with all scaled surfaces, sufficient solution may be introduced to substantially fill the system, i.e., the boiler, the risers and the steam drum. The solution may then be slowly circulated with the pumps to contact all surfaces including the downcomers. Moderate temperatures are suitable for this cleaning step. If the scale is light or freshly deposited, room temperature treatment is adequate. With heavier or older scales, it is usually...
preferable although not essential to heat the solution for most rapid cleaning. In this case, temperatures from about 140° F. up to the boiling point of the solution are most effective. If desired, temperatures above the atmospheric boiling point may be employed by operating under pressure. However, this expedient is generally unnecessary. It is noteworthy that the process is so safe that no corrosion inhibitor is normally required, even at the higher temperatures. The progress of the cleaning is conveniently followed by withdrawing liquid samples periodically and assaying for iron according to any of the standard procedures. When the iron content of the solution becomes substantially constant the first phase of the operation may be regarded as substantially complete. Generally this will be found to occur after about one to three hours at temperatures of about 140–160° F.

 Naturally, if the unit is small and heavily scaled, it is possible that the volume of cleaning solution which it can hold will become exhausted before all of the iron oxides have been removed. This situation is readily detected, since one mole of iron is complexed by each mole of citrate, i.e. 56 parts by weight of iron to each 192 parts by weight of citric acid. Therefore, if the molar iron content of the solution levels off at a value corresponding to the original molar concentration of citric acid introduced, it is possible that the iron oxide has been incompletely removed. If this is the case, it is safest to introduce additional citric acid and nitrogen base into the solution and repeat the procedure. Ordinarily, however, it is possible to estimate from past experience the amount of iron oxides to be removed, and to make due provision by employing a suitably high level of citrate where such will be required.

 During the dissolution of iron oxides in the acidic cleaning step elemental copper will usually plate out on the bare metal surfaces exposed to the solution. (This redeposition would occur even should such copper complexing agents as thiourea or diethylenetriourea be incorporated in the solution. Moreover, such agents may sometimes accelerate attack of bare metal by acids.) However, in this phase of the operation copper plating is advantageous. The copper acts as a protective film on the steel, preventing even slight attack by the mild solution, and insuring that the citrate will react only with the oxide scale. Accordingly, cleaning time and citrate requirement are kept to a minimum, and bare metal is protected. However, as has already been pointed out, the copper film must be removed before putting the unit back in service. This is readily accomplished in the second or final cleaning step.

**Alkaline step**—In this step I utilize the same cleaning solution, merely raising the pH with one of the nitrogen bases already described, without even draining the boiler. Triethanolamine is a particularly convenient base to work with, since its low vapor pressure avoids fumes at the higher pH's. However, ammonia is eminently suitable, and economy may often dictate its use. The base is conveniently introduced in water solution, which may be pumped into the boiler. This will displace a small portion of the cleaning solution to waste, but the loss is inconsequential. The pH should be adjusted to between about 8 and about 10, preferably about pH 9. If mineral acid had been used in the first step, adherent iron oxides would reprecipitate upon thus raising the pH to the effective range.

 Particularly good results are obtained when the alkaline step is begun with a free citrate concentration corresponding to about 0.5% w/v or more citric acid. By "free citrate" I refer to that which is not complexed with iron. The free citrate concentration is readily calculated from the citric acid originally introduced and the final iron content of the solution, as previously described. If this concentration has dropped below a value corresponding to about 0.5% citric acid, additional citric acid may be introduced at the start of the alkaline step. While this is by no means essential to the successful operation of my new process, it has been observed to provide clear solutions free of the sediment which is sometimes encountered.

 This facilitates rapid and complete rinsing of the equipment after cleaning. Since free citrate concentrations corresponding to more than about 1.5% w/v citric acid offer no added advantage, levels between about 0.5 and 1.5% will usually be preferred in the interest of economy.

 During the alkaline cleaning step, addition of an oxidizing agent is often beneficial in increasing the reaction rate. Iron oxides, for example, are oxidized by hypochlorite, hydrogen peroxide, and potassium permanganate. Air or oxygen are eminently suitable and are readily introduced by injection into the solution through a sparger or bubbler during alkaline cleaning. Among other gaseous oxidants which may be employed in the same manner is nitrogen tetraoxide. Where it is inconvenient to provide a sparger, the same advantage may be obtained by incorporating liquid or solid oxidants, such as potassium permanganate or nitrophensulfonyc acid sodium, in the cleaning solution. Particularly convenient and effective are water-soluble inorganic salts, especially permanglates, perchlorates, bromates or nitrates. Suitable salts include, for example, the chloride, the nitrate, potassium and ammonium salts. Very little of such oxidant is required for the desired beneficial effect, ordinarily about one part by weight for each part by weight of copper to be removed.

 The temperature for this step is not critical. Room temperature (or even lower) is quite suitable. Intermediate temperatures up to boiling may be used if desired. The solution at pH 8–10 is best circulated as before, until standard analysis of liquid samples indicates that the copper content is substantially constant. With air or other added oxidant one to two hours will usually suffice.

 At this time the cleaning solution may be drained to waste and the unit rinsed with water. The treated surfaces are left silvery grey in color, scale-and copper-free, and ready for return to service. The entire operation usually requires only about 5–8 hours, even for a large unit.

 The following examples are provided for illustrative purposes and should not be interpreted as limiting the invention, the scope of which is defined by the appended claims.

**Example 1**

A conventional controlled circulation boiler having a capacity of 1.5 million lbs. steam per hour at about 2000 p.s.i. is shut down to remove operational deposits from the inner surfaces of the steel boiler, steam drum, risers and downcomer. The deposits are estimated to contain about 1000 lbs. of FeO, and about 50–100 lbs. of copper picked up from the condenser. The boiler water temperature is allowed to cool to 200° F, while a solution of 3000 lbs. citric acid in about 3000 gallons of water is prepared in a separate tank and adjusted to about pH 2.7 with aqueous ammonia. This solution is then pumped into the bottom of the boiler, displacing an equal amount of water which is permitted to overflow to waste from the steam drum. The diluted cleaning solution in the boiler has a volume of about 22,000 gallons and a pH of approximately 3.7.

The boiler pumps are operated to slowly circulate the solution through the system (about 1 ft/sec., in the tubes) while periodic samples are withdrawn for iron analysis. After about two hours the iron content of the cleaning solution has become substantially constant at a value corresponding to about 500 pounds of dissolved iron, and the solution temperature has dropped to about 160° F.

Since the iron analysis shows that substantially all of the citrate present is complexed with iron, an additional 2000 pounds of citric acid is dissolved in about 3000 gallons of water and pumped into the solution already in the boiler, together with sufficient aqua ammonia to
provide a pH of about 10 in the total mixture. This operation requires about 15 minutes. At this time, aeration of the solution is begun by admitting air from a compressor through a perforated pipe installed inside the boiler and connected to the boiler blowdown valve. The pipe acts as a sparger, facilitating good distribution of the injected air. The solution is slowly circulated by means of the boiler pumps and aeration is continued without applying heat. After an hour the copper content of the cleaning solution has leveled off at a value corresponding to approximately 80 pounds of dissolved copper.

The solution is now drained to waste and the system is rinsed with water, an operation that requires about an hour. Inspection of the interior of the boiler and steam drum reveals that the surfaces are pale silvery gray and free from traces of scale and foreign matter. No tendency for after-rusting is noted.

Example II

A mild steel boiler tube sample, coated with a scale which proves upon analysis to contain magnetite, Fe₃O₄, copper, and oxides of copper, is immersed in a 1% w/v aqueous citric acid solution previously adjusted to pH 2.5 with triethanolamine, and the solution is heated at about 140° F. with gentle agitation for about 3 hours. At this time the iron content of the solution is substantially constant at a level corresponding to the original molar concentration of citric acid. The surface is free of scale and coated with copper.

After cooling to room temperature sufficient triethanolamine is added to raise the pH to about 8, and oxygen is bubbled through the solution with gentle agitation for about 3 hours. At the conclusion the steel is rinsed with water and found to have a scale-free silvery finish.

Example III

A steel surface having a freshly deposited, light scale of copper-containing iron oxide is immersed in a monoammonium citrate solution equivalent in concentration to 5% w/v, citric acid and gently agitated at room temperature until the scale is removed and the surface is plated with copper. The pH is now adjusted to about 9 with monoethanolamine and the solution is boiled at this pH until the copper has all dissolved. The cleaned surface closely resembles that of Example II.

Example IV

A number of scaled tube samples similar to that of Example II are immersed in 1.5% citric acid solutions which have been adjusted to pH 5 with a series of amines:

- Trimethylamine
- Diethylamine
- Diethanolamine
- Isobutyramine
- n-Amylamine

Each solution with its immersed plate is boiled until the scale is removed and the plates covered with a light copper film. The molar iron content of the solutions corresponds closely to the citrate introduced. Each pH is now adjusted to about 8 with the amine previously employed. Air is then bubbled into the solutions with gentle stirring until the copper has dissolved and clean metal surface exposed.

Example V

A number of scaled boiler tube samples similar to those of Examples II and IV are immersed in 3% w/v. citric acid solutions adjusted to pH 4 with ammonia. After about 2 hours at 50° F. the scale has been removed and the iron analysis indicates that citrate corresponding to about 1.5% citric acid remains uncomplexed.

Each solution is now adjusted to about pH 9 with ammonia, and to each is added 0.1% w/v. of one of a series of oxidizing agents:

- Ammonium persulfate
- Potassium perchlorate
- Potassium bromate
- Sodium nitrite
- Potassium permanganate
- Nitrophenyl sulfonic acid sodium salt

The various solutions are heated at 140° F. with gentle agitation until the copper plating has dissolved.

What is claimed is:

1. A process for the removal of copper-containing iron oxide scale from metal surfaces which comprises contacting said surfaces with an aqueous solution containing at least about 1% w/v. citric acid together with sufficient base to provide a pH between about 2.5 and about 5, said base being selected from the group consisting of ammonia, an unsubstituted ethanamine and a water-soluble aliphatic hydrocarbon amine, continuing said contact until the iron content of said solution becomes substantially constant, subsequently adjusting the pH of said solution with one of said bases to a value between about 8 and about 10, and maintaining the pH within said alkaline range while continuing said contact until the copper content of said solution becomes substantially constant.

2. A process as in claim 1 wherein said base is ammonia.

3. A process as in claim 1 wherein said base is triethanolamine.

4. A process as in claim 1 wherein said acidic cleaning step is conducted at a temperature between about 140° F. and the boiling point of said solution.

5. A process as in claim 1 wherein said alkaline cleaning step is conducted in the presence of an added oxidizing agent.

6. A process as in claim 5 wherein said agent is air injected into said solution.

7. A process as in claim 5 wherein said agent is a water-soluble inorganic salt.

8. A process as in claim 7 wherein said salt is selected from the group consisting of persulfates, perchlorates, bromates and nitrates.

9. A process for the removal of copper-containing iron oxide scale from metal surfaces which comprises contacting said surfaces with an aqueous monoammonium citrate solution at a concentration equivalent to between about 1.5 and about 3% w/v. citric acid and a temperature between about 140° F. and the boiling point of said solution until the iron content of said solution becomes substantially constant, subsequently adjusting said solution with ammonia to a pH between about 8 and about 10 at a free citrate concentration equivalent to at least about 0.5% w/v. citric acid, and maintaining said alkaline solution in contact with said surfaces while injecting air until the copper content of said solution becomes substantially constant.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Inventor</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>865,700</td>
<td>Hernsheim</td>
<td>Sept. 10, 1907</td>
</tr>
<tr>
<td>2,567,825</td>
<td>Alquist et al.</td>
<td>Sept. 11, 1951</td>
</tr>
<tr>
<td>2,676,900</td>
<td>Spenel et al.</td>
<td>Apr. 27, 1954</td>
</tr>
<tr>
<td>2,817,606</td>
<td>Barrett</td>
<td>Dec. 24, 1957</td>
</tr>
<tr>
<td>2,995,477</td>
<td>Florence</td>
<td>Aug. 8, 1961</td>
</tr>
<tr>
<td>3,000,767</td>
<td>Elliott</td>
<td>Sept. 19, 1961</td>
</tr>
<tr>
<td>3,003,899</td>
<td>Eberhard</td>
<td>Oct. 10, 1961</td>
</tr>
<tr>
<td>3,013,909</td>
<td>Pancer</td>
<td>Dec. 19, 1961</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>602,414</td>
<td>Canada</td>
<td>July 26, 1960</td>
</tr>
</tbody>
</table>