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PASSIVATION OF FERROUS METAL SURFACE

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The invention relates to an improvement in the method of passivation of a ferrous metal surface, e.g., steel, especially following removal of metallic copper from the surface.

The art of cleaning steam boilers and associated piping and vessels has progressed from the use of highly acidic solutions for the dissolution of hard water scale and rust or magnetite to the current use of materials which complex iron or calcium and magnesium as well. Solutions of complexing agents do not rely on hydrogen ions to accomplish scale loosening or solution. In fact, such cleaning solutions now employed are often made alkaline by the addition of ammonia.

A common problem arising in the cleaning of ferrous metal equipment having some copper or copper alloy portions, e.g., heat exchanger sections in a boiler used in a power generating plant, lies in the reduction of dissolved copper by newly cleaned ferrous metal surfaces with concomitant deposition of the copper on the ferrous metal surfaces. Such plated copper must be very thoroughly removed else deleterious bimetallic couple corrosion will take place when the equipment is placed back in service.

One solution to this problem has been to introduce an oxidizing agent into the cleaning solution after substantially complete removal of scale and iron oxides. The copper is oxidized and stripped from the ferrous metal surface, the more readily if the solution contains materials capable of complexing or chelating copper, e.g., ammonia or the ferric or ferrous chelates of the ammonium salt of ethylenediaminetetraacetic acid.

Suitable oxidizing agents are ferric citrate, the ferric chelate of ethylenediaminetetraacetic acid and its salts, sodium nitrite, and, oxygen or air bubbled through the cleaning solution. Also usable are soluble ferric salts, nitric acid, readily soluble tungstates and molybdates, and ammonium persulfate and ammonium bromate.

Upon employing additional oxidizing agent beyond that required for copper stripping, it has been found that the ferrous metal surface is often brought to a passive condition in which the metal appears clean and bright, and the metal does not oxidize or rust readily for a time. However, not infrequently the ferrous metal surface has failed to become passive, and in fact, has carried a thin film of yellow surface oxidation at the conclusion of the cleaning operation. The cause of the seemingly random occurrence of this condition has not been understood and so it has not been possible to avoid the condition with certainty.

It is therefore a principal object of this invention to provide a positive method of passivating a ferrous metal surface following stripping of copper with an oxidizing agent.

An even broader object of the invention is to provide an improved method of passivating any clean and bright ferrous metal surface.

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

It has been discovered that upon monitoring the oxidation potential of a cleaning solution during the addition of oxidizing agent in the passivation of a ferrous metal surface, the cleaning solution having a pH of about 7.5 to 10, and upon stopping the addition of oxidizing agent when the oxidation potential is in the range of about 250 to 175 millivolts, the ferrous metal surface is assuredly brought to a passive condition and exhibits a bright metallic appearance.

The theory of the present method is not entirely understood, but it is evident that the ferrous metal surface is brought to the desired condition when there obtains an appropriate ratio of oxidized ion species, e.g., ferric ion species, to reduced ion species such as ferrous ion species in the solution used for cleaning and/or passivating. The ratio of ferric ion species to ferrous ion species may be measured in any suitable manner. The most convenient way is simply to measure the oxidation potential of the solution. Both a saturated calomel electrode (S.C.E.) and one of a platinum or a ferrous metal electrode are inserted into the solution, employed for cleaning and/or passivating, and are interconnected through a high impedance voltmeter, conveniently, a digital voltmeter. It is generally desirable to employ a ferrous metal electrode having the same or a similar composition as the ferrous metal surface being treated since such an electrode will, in general, more accurately reflect the condition of the treated surface. However, if the metal electrode cannot conveniently be of the same composition as the metal being passivated, a platinum electrode is more likely to give the most reliable determinations. Under a given set of conditions, a platinum electrode versus a saturated calomel electrode will exhibit about 10 millivolts less potential difference than the iron-saturated calomel couple.

In carrying out the method of the present invention immediately following stripping of copper, and generally also following dissolution of all scale deposits, the cleaning solution is brought to a temperature less than about 195° F., usually to less than 180° F. and preferably to less than about 160° F., but above about 100° F. The optimum temperature is approximately 140° F.

The pH of the solution is adjusted, if necessary, to an alkaline value, preferably in the range of from about 7.5 to about 10. In the alkaline pH range, iron solutions in contact with ferrous metal exhibit broader more reproducible rest potentials, or plateaus on polarographic examination, than at lower pH values. During the oxidizing step, the ferrous substrate would be adversely affected if the solution pH were allowed to drop below about 7.0.

In solutions used for stripping copper there will generally be present ferric citrate, or an ammonia, amine or alkanolamine salt of a ferric chelate of a polycarboxylic acid chelating agent. Such iron complexes or chelates readily react with copper to oxidize it, leaving ferrous species in solution. Oxidation of the copper is effected by the addition of an oxidizing agent which generally reacts most readily with such ferrous species which in turn oxidize metallic copper. Most conveniently used as an oxidizing agent is air which is simply bubbled through the solution, substantially does not change the liquid volume, causes little loss of ammonia or volatile amine and builds up no residue of salts or foreign ion species.

Suitable polycarboxylic acid chelating agents include the alkylene polyamine polyacetic acids of the formula

$$(HOOCCH_2)_2N[(CH_2)_nNCH_2COOH]_mCH_2COOH$$

wherein n and m may each independently be 1, 2, 3, or 4, 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-hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid, and mixtures thereof.

Examples of suitable paired combinations of ammonia, amines, and alkanolamines with such polycarboxylic acids are listed in the following table.

Amines:	Used with 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(beta-hydroxyethyl) glycine.
Ammonia	Tetramethylenediamine-N,N,N',N'-tetraacetic acid.
Ammonia	(2-hydroxyethylimino) diacetic acid.

Generally about 0.5 to about a 40 weight percent aqueous solution of iron complexing or chelating agent is suitable for stripping copper and passivating. At least a 2 weight percent solution is preferred and more preferably a 4 to about 20 percent solution. Typically a 6 to 12 percent solution is used in commercial type operations. To avoid undue attack on the ferrous metal substrate, the iron complexing or chelating agent is essentially in the condition of holding 60 to 97 percent of the theoretical maximum amount of iron.

While the iron complexing or chelating agent may be reacted or "spent" with iron powder to exhaust the requisite proportion of its chelating power, as a practical matter, the iron complexing or chelating agent is normally used in the requisite amounts in a prior cleaning step, involving the removal of iron oxide-containing scale, that the desired degree of binding or chelating is achieved preparatory to copper stripping and/or passivating.

Addition of the oxidizing agent selected is continued after stripping of the copper in order to effect passivation with the solution pH and temperature adjusted as described. As oxidizing agent is added, the solution oxidation potential falls. Passivation, as determined by visual examination of exposed specimens, or coupons, commences on at least part of the steel substrate when the oxidation potential reaches about 250 millivolts (iron vs. S.C.E.) or 240 millivolts (platinum vs. S.C.E.) and diminishes and disappears after about 175 millivolts (iron vs. S.C.E.) or 165 millivolts (platinum vs. S.C.E.). Generally good passivation is obtained with greater assurance when oxidation is stopped when the solution oxidation potential is in the range of about 210 to 180 millivolts as determined by the ferrous metal electrode versus saturated calomel electrode. Accuracy and assurance are also increased by adding the oxidizing agent slowly enough for prompt reaction and prompt indication of the state of the solution as shown by the oxidation potential readings; thus "overshooting" the desired potential is avoided. Slower rates of addition have no noticeable effect on the degree of passivation. The temperature of the solution within the range of 100 to 180° F. has very little effect on the oxidation potential readings, the desired terminal voltage varying not more than 10 millivolts at the extremes of this range.

When the solution oxidation potential has reached a predetermined value in the stated range, the addition of oxidizing agent is stopped. If there is any time lag in reaction, as with residual copper deposits, the oxidation potential will climb again within a few minutes and further oxidizing agent is required to reach the predetermined oxidation potential. Once the potential becomes stable, the solution is promptly withdrawn from the vessel or equipment being treated, and the vessel or equipment rinsed with water at ambient room temperature. The cleaned ferrous metal surfaces are clean, bright and passive, and ready to be returned to service.

The passivation process of the invention need not be carried out following copper stripping where the equipment does not contain, and has not just been cleaned of copper. Where copper is not involved, the vessel or equipment is cleaned so as to provide entirely clean and bright surfaces throughout. The vessel or equipment is then substantially filled with an aqueous solution containing an electrolyte such as one or more of the complexing or chelating agents listed hereinabove. It is highly desirable that such complexing or chelating agent has been spent in some manner to hold at least 60 percent by weight of the theoretical amount of dissolved iron. The pH is adjusted to an alkaline value, if necessary, preferably in the range of 7.5 to 10, and maintained at an alkaline pH. The temperature is maintained at less than about 195° F., usually at less than 180° F. and preferably at less than 160° F., but above about 100° F. during the addition of one of the above listed oxidizing agents, conveniently, air. The oxidation potential of the solution is monitored as described hereinbefore, and the addition of oxidizing agent is stopped when the oxidation state of the system, as reflected by the ratio of ferric ion to ferrous ion species, corresponds to an oxidation potential in the range of about 250 to 175 millivolts, and preferably about 210 to 180 millivolts (Fe vs. S.C.E.). The solution is then drained, and the vessel or equipment rinsed with clean water.

Examples

The following examples are to be considered illustrative and not limitative of the scope of the invention.

(I). In each of a series of runs illustrating the practice of the invention ammoniated ethylenediaminetetraacetic acid (ammoniated EDTA) and water were added to a small simulated boiler having a steel pot connected to a glass header, disposed above the steel pot, by means of two foreshortened replaceable steel boiler tubes and a glass downcomer, all three tubes being connected in parallel. The boiler was also fitted with an iron electrode, a platinum electrode, and a saturated calomel electrode. Sufficient ammoniated EDTA solution was used to bring the liquid level well up into the glass header.

The boiler tubes, in each case, were cleaned by bringing the boiler to 212° F. for a short time. Then enough copper oxide (CuO) was added to the solution to bring the dissolved copper level, on a theoretical basis, to 0.06 percent by weight of copper. This solution was circulated until all the copper oxide dissolved and plated on the steel substrate. The solution was then spent to the desired level with iron powder and cooled, after which the pH was adjusted to about 9 with a concentrated aqueous solution of ammonia.

Air blowing was then carried out to remove plated copper and to bring the steel substrate to a passive condition. Air was admitted to the steel pot through a fritted glass plug. The pH remained alkaline during each test. At the termination of the air blowing step the oxidation potential of the solution was recorded. The solution was drained out to permit disassembly of the boiler and inspection of the boiler tubes.

The solution concentrations, temperatures, and terminal oxidation potentials and the condition of the treated boiler tubes are summarized in the following table.

TABLE I.—PASSIVATION OBTAINED UNDER VARIOUS CONDITIONS

Run No.	Concentration of chelating agent, weight percent	Degree of spentness, percent	Temp., ° F.	Potential at end of air blowing Mv. (Fe vs. S.C.E.)	Potential at end of air blowing Mv. (Pt vs. S.C.E.)	Degree of passivation obtained
1	12.5	79	170	242	----------	Fair.
2	21.5	76	192	214	----------	Fair to poor.
3	12.5	96	192	242	222	Good to fair.
4	12.5	84.6	185	188	182	Good.
5	15	92	185	200	198	Good, some small local deposits of red iron oxides.
6	18.5	79	185	201	198	Good to fair.
7	10	70	185	200	195	Fair.
8	10	90.2	175	200	194	Good.
9	10	64	175	200	194	Good to fair.
10	10	79	175	199	193	Do.
11	10	71	162	198	190	Fair.
12	10	96	162	200	197	Good to fair.
13	12.1	69	140	203	198	Good.
14	10	97.5	140	195	190	Do.
15	12.5	92	142	200	199	Fair.
16	10	95	130	199	197	Good.
17	10	93	100	199	195	Do.
18	10	69	100	197	187	Do.
19	10	58	100	199	195	Good to fair.

Mv.=millivolts.
S.C.E.=saturated calomel electrode.
Chelating agent=ammoniated ethylenediaminetetraacetic acid.

(II) In each of additional runs according to the present invention, a simulated boiler such as that described above was charged with a 10 percent solution of ammoniated EDTA, heated to 212° F. for a short time, and then copper oxide was introduced to cause copper to plate out on the steel substrate. The solution was spent to a predetermined level with iron powder and cooled after which the pH was adjusted to a level between about 9.1 and 9.3 with aqueous ammonium hydroxide. Air blowing was carried out to strip off plated copper and to bring the steel substrate to a passive condition. In Table II following, solution concentrations, temperatures, initial and final pH levels and terminal solution potential values are summarized.

TABLE II.—EFFECT OF AIR BLOWING ON pH

Run No.	Weight percent of chelating agent	Degree of spentness	Temp., ° F.	Potential at end of air blowing, mv. Fe vs. S.C.E.	Potential at end of air blowing, mv. Pt vs. S.C.E.	pH Before blowing	pH After blowing	Condition of tubes
20	6.25	80	175	210	177	9.1	8.6	Passive.
21	6.25	82	160	----------	184	9.3	9.3	Do.
22	6.9	85	170	226	190	9.3	9.1	Do.
23	3.9	87	168	175	168	9.3	9.05	Do.

The data in the table shows that there is a negligible drop in pH due to loss of ammonia during a typical air-blowing step.

(III) The following tests illustrate the deleterious effects upon carrying the oxidation step too far following stripping of copper from steel substrate.

(1) Sufficient ammonium hydroxide was added to a 5 percent aqueous citric acid solution contained in a simulated boiler such as that described hereinabove to reduce the acidity of the solution to pH 5. The solution was "spent" on iron powder at 185° F. after which the pH was adjusted to a value of 9 by the further addition of ammonium hydroxide. While the solution temperature was maintained at 185° F., air was rapidly introduced into the solution through a fritted glass tube. Throughout the air-blowing period the oxidation potential of the solution was measured using a ferrous metal electrode formed of 1010 Steel (AISI designation) versus a saturated calomel electrode.

The initial potential of 812 millivolts (mv.) became smaller as air was bubbled through the solution. At 248 mv., a copper plated steel coupon suspended in the boiler was stripped of copper. Once the potential had fallen to 212 mv., it dropped suddenly to 12 mv. and the surface of the steel specimens suspended in the boiler began oxidizing. Upon removing the specimens from the solution severe local after-rusting occurred.

(2) On repeating the test of part (1), immediately above, the initial potential was found to be 808 mv. Copper stripping was substantially complete at 315 mv. The oxidation potential subsequently fell to 46 mv. At this stage of the process steel surfaces were deteriorating badly. Steel specimens removed from the boiler exhibited severe local after rusting.

(3) The test of part (1) above was repeated but with a slower rate of air addition. With changes taking place more slowly, it was observed that surface deterioration of steel specimens suspended in the boiler became noticeable when the oxidation potential of the solution had decreased to about 180 mv.

(IV) A series of aqueous sodium nitrite solutions was prepared and employed respectively in using the simulated boiler described hereinabove. In each case steel coupons were suspended in water in the boiler during the addition of the aqueous sodium nitrite solution. Sodium nitrite addition was carried out under various temperature conditions and terminated at various potentials.

The steel coupons were removed, rinsed, dried, and subjected to visual examination. Then the coupons were stored 16 hours at ambient room temperature under conditions of 40 percent relative humidity before making a second visual examination to determine surface condition.

Solution concentrations, temperatures, terminal potentials, and the results of visual examinations are summarized in the following table.

TABLE III.—RESULTS OF PASSIVATION WITH $NaNO_2$ SOLUTION

Run No.	Solution Conc., Wt. %	Temp., ° F.	Terminal Potential, Mv. (Fe vs. SCE)	Passivation	
				Initial Inspection	Inspection After 16 hrs.
Comparison	10	25	132	Poor	Poor.
Do	10	177	123	Very poor	Very poor.
24	5	25	197	Good	Good.
25	5	177	181	Good to fair	Do.
26	2.5	25	230	Very good	Very good.
27	2.5	177	228	do	Do.
28	1.25	25	184	Good to fair	Good.
Comparison	1.25	177	167	Fair to poor	Fair to poor.

Solution≡aqueous $NaNO_2$ solution.
Mv.=millivolts.
Fe=steel.
S.C.E.=saturated calomel electrode.

The process 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 appended claims.

What is claimed is:

1. In the method of passivating a ferrous metal surface in contact with an aqueous solution exhibiting an alkaline pH and containing both ferric and ferrous ion species in which additions of oxidizing agent are made to the said aqueous solution, the improvement which comprises: monitoring the state of oxidation exhibited by the ferric iron concentration-ferrous iron concentration ratio during the addition of oxidizing agent and stopping such addition when the oxidation potential of the said aqueous solution is in the range of 250 to 175 millivolts as measured with a ferrous metal electrode with reference to a saturated calomel electrode.

2. The method as in claim **1**, in which the process is carried out until the oxidation potential of the solution is in the range of about 210 to 180 millivolts as measured with a ferrous metal electrode with reference to a saturated calomel electrode.

3. The method as in claim **1** in which the said aqueous solution is maintained at a temperature less than about 180° F. and the said solution contains from 0.5 to about 40 percent by weight of an iron chelating agent, said iron chelating agent having dissolved iron bound thereto to the extent of 60 to 97 percent of its maximum theoretical chelating capacity.

4. The method as in claim **3** in which the chelating agent is ammoniated or amminated EDTA.

5. The method as in claim **3** in which the chelating agent is ammoniated citric acid.

6. The method as in claim **3** in which the chelating agent is a member of the group consisting of an ammonia, amine or alkanolamine salt of a polycarboxylic acid chelating agent.

7. The method as in claim **1** in which the ferrous metal surface has been freshly stripped of copper metal deposit.

8. The method as in claim **1** in which the oxidizing agent is selected from the group consisting of air, and from aqueous solutions of one of, HNO_3, $NaNO_2$, K_2CrO_4, alkali metal and alkaline earth metal molybdates, tungstates, ferric citrate, ferric nitrite or an ammonia, amine or alkanolamine salt of a ferric chelate of a polycarboxylic acid chelating agent.

9. The method as in claim **1** wherein the oxidizing agent is added while the aqueous solution is at a temperature less than about 160° F. but above 100° F.

10. In the method of removing metallic copper from a ferrous metal surface, and thereafter passivating the ferrous metal surface, in which method copper removal is effected by oxidation of the metallic copper by means of addition of an oxidizing agent, the improvement which comprises; monitoring the ratio of ferric ion to ferrous ion species in the solution, and stopping the addition of oxidizing agent when 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.

11. The method as in claim **10** in which a platinum electrode is used in place of a ferrous metal electrode.

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