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PATENT SPECIFICATION

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The Inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act 1949 is: FRED NORMAN TEUMAC, 2227 Rocky Knoll Drive, Charlotte, County of Mecklenburg, State of North Carolina, United States of America, a citizen of the United States of America.

COMPLETE SPECIFICATION

Process for the Passivation of Ferrous Metal Surface

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

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 the cations of metals such as iron, calcium and magnesium. 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 and amines.

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.

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 other soluble ferric salts, nitric acid, readily soluble tungstates and molybdates, 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 occasionally 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 has now been found, and the discovery forms the basis for the present invention, that monitoring the oxidation potential of the cleaning solution to a value of 175 to 250 millivolts when measured with iron and saturated calomel at a temperature from 37.8° C. and 90.5° C. the ferrous metal surface is brought to a bright passive condition.

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, to reduced ion species such as ferrous ion in the solution used for cleaning and 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 a platinum or ferrous metal electrode are inserted into the solution, employed for cleaning and 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.

The present invention, therefore, relates to a process for passivating a ferrous metal surface which comprises contacting the surface with an aqueous alkaline solution having an oxidation potential of 175 to 250 millivolts when measured between iron and saturated calomel electrodes at a temperature between 37.8° C. and 90.5° C. and which solution contains ferric and ferrous salts of one or more aminocarboxylic acid chelating agents. The process may very conveniently follow a cleaning operation in which the passivating solution of the invention is formed in place by the reaction of an alkaline solution containing aminocarboxylic acid chelating agents with scale and oxide residues on the surface, the oxidation potential being controlled as required by the addition of an oxidizing agent. Metallic copper, when present, is dissolved as the oxidation reaction proceeds.

Preferably, in the process of the present invention, the aminocarboxylic acid chelating agent is a polyaminopolycarboxylic acid chelating agent.

The passivation is effected at a temperature in the range from 37.8° C. to 90.5° C. generally with a solution containing from 0.5 to 40 weight percent of the combined ferric and ferrous salts. Preferably 60 to 97 percent of the metal chelating capacity of the aminocarboxylic acid chelating agent is occupied by ferric and ferrous ions. It is particularly advantageous where a cleaning step precedes the passivating step to employ an alkaline solution containing one or more aminocarboxylic acid chelating agents and ammonia, amine, polyamine, or polyalkylene polyamine in a proportion to render the solution alkaline. The oxidizing agent generally employed is oxygen or air.

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 195° F. (90.5° C.) usually to less than 180° F. (82° C.) and preferably to less than 160° F. (71° C.) but above 100° F. (37.8° C.). The optimum temperature is approximately 140° F. (60° C.). The pH of the solution is adjusted, if necessary, to an alkaline value, preferably in the range of from 7.5 to 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 an aminocarboxylic 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 aminocarboxylic acid chelating agents include the alkylene polyamine polyacetic acids of the formula

$$(HOOCCH_2)_2\text{-}N[(CH_2)_nN(CH_2COOH)]_mCH_2COOH,$$

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 aminocarboxylic acids are listed in the following table.

Amines	Used With: Aminocarboxylic 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-hydroxethyl) glycine
Ammonia	Tetramethylenediamine-N,N,N′,N′-tetraacetic acid
Ammonia	(2-hydroxyethylimino) diacetic acid

Generally 0.5 to a 40 weight percent aqueous solution of iron complexing or chelating agent is suitable for stripping copper and passivating ferrous metal surfaces. At least a 2 weight percent solution is preferred and more preferably a 4 to 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 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 195° F. (90.5° C.), usually at less than 180°F. (82° C.) and preferably at less than 160° F. (71° C.) but above 100° F. (37.8° C.) 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 250 to 175 millivolts, and preferably 210 to 180 millivolts (Fe v. S.C.E.). The solution is then drained, and the vessel or equipment rinsed with clean water.

EXAMPLES

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. (100° C.) 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 the copper 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 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 %	Degree of Spentness %	Temp. °F.	Temp. °C.	Potential at end of Air Blowing mv. (Fe vs. SCE)	Potential at end of Air Blowing Mv. (Pt vs. SCE)	Degree of Passivation Obtained
1	12.5	79	170	76.5	242	—	Fair
2	21.5	76	192	89	214	—	Fair to poor
3	12.5	96	192	89	242	222	Good to fair
4	12.5	84.6	185	85	188	182	Good
5	15	92	185	85	200	198	Good, some small local deposits of red iron oxides
6	18.5	79	185	85	201	198	Good to fair
7	10	70	185	85	200	195	Fair
8	10	90.2	175	79.4	200	194	Good
9	10	64	175	79.4	200	194	Good to fair
10	10	79	175	79.4	199	193	Good to fair
11	10	71	162	72	198	190	Fair
12	10	96	162	72	200	197	Good to fair

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TABLE I (Continued)

Passivation Obtained Under Various Conditions

Run No.	Concentration of Chelating Agent, Weight %	Degree of Spentness %	Temp.		Potential at end of Air Blowing		Degree of Passivation Obtained
			°F.	°C.	mv. (Fe vs. SCE)	mv. (Pt vs. SCE)	
13	12.1	69	140	60	203	198	Good
14	10	97.5	140	60	195	190	Good
15	12.5	92	142	61	200	199	Fair
16	10	95	130	54.4	199	197	Good
17	10	93	100	37.8	199	195	Good
18	10	69	100	37.8	197	187	Good
19	10	58	100	37.8	199	195	Good to fair

mv. = millivolts

SCE = 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. (100° C.) 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 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 % of Chelating Agent	Degree of Spentness	Temp.		Potential at end of air blowing, mv.		pH		Condition of Tubes
			°F.	°C.	Fe vs. SCE	Pt vs. SCE	Before Blowing	After Blowing	
20	6.25	80	175	79.4	210	177	9.1	8.6	Passive
21	6.25	82	160	71	—	184	9.3	9.3	Passive
22	6.9	85	170	76.6	226	190	9.3	9.1	Passive
23	3.9	87	168	75.6	175	168	9.3	9.05	Passive

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. (85° C.) 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., (85° C.) 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.	Temp. °C.	Terminal Potential, mv. (Fe v. SCE)	Passivation: Initial Inspection	Passivation: Inspection After 16 Hours
Comparison	10	25	−4	132	Poor	Poor
Comparison	10	177	80.6	123	Very poor	Very poor
24	5	25	−4	197	Good	Good
25	5	177	80.6	181	Good to fair	Good
26	2.5	25	−4	230	Very good	Very good
27	2.5	177	80.6	228	Very good	Very good
28	1.25	25	−4	184	Good to fair	Good
Comparison	1.25	177	80.6	167	Fair to poor	Fair to poor

Solution = aqueous $NaNO_2$ solution

mv. = millivolts

Fe = steel

SCE = saturated calomel electrode

WHAT WE CLAIM IS:—

1. A process for passivating a ferrous metal surface which comprises contacting the surface with an aqueous alkaline solution having an oxidation potential of 175 to 250 millivolts when measured between iron and saturated calomel electrodes at a temperature between 37.8° and 90.5° C. and containing ferric and ferrous salts of one or more aminocarboxylic acid chelating agents.

2. A process as claimed in claim 1 wherein the aminocarboxylic acid chelating agent(s) employed is polyaminopolycarboxylic acid chelating agent.

3. A process as claimed in claim 1 or claim 2 wherein the passivating solution is formed in place by the reaction of an alkaline solution containing aminocarboxylic acid chelating agents with scale and oxide residues on the surface, the oxidization potential being controlled as required by the addition of an oxidizing agent.

4. A process as claimed in claim 2 or claim 3 wherein metallic copper is solubilized during the oxidation step.

5. A process as claimed in any one of claims 1 to 3 wherein the contacting treatment is carried out at a temperature of 60° C.

6. A process as claimed in any one of the preceding claims wherein the alkaline solution contains from 0.5 to 40 weight per cent of the combined ferric and ferrous salts of the complexing or chelating agent.

7. A process as claimed in any one of the preceding claims wherein from 60 to 97 per cent of the metal chelating capacity of the polycarboxylic acid chelating agent is occupied by ferric and ferrous ions.

8. A process as claimed in any one of claims 2 to 7 wherein the alkaline solution contains one or more polycarboxylic acids and ammonia, amine, polyamine, or polyalkylene polyamine in a proportion to render the solution alkaline.

9. A process as claimed in any one of claims 2 to 8 wherein the oxidizing agent is oxygen.

10. A process as claimed in any one of the preceding claims wherein the aqueous alkaline solution is maintained at a pH from 7.5 to 10 during the contacting treatment.

11. A process as claimed in any one of claims 2 to 10 wherein the polycarboxylic acid has the formula

$$(HOOCCH_2)_2\text{-}N[(CH_2)_nN(CH_2COOH)]_mCH_2COOH,$$

wherein n and m are each independently 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.

12. A process for passivating ferrous metal surfaces substantially as hereinbefore described with reference to the specific Examples.

13. Ferrous metal surfaces whenever passivated by the process claimed in any one of the preceding claims.

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