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METHOD OF FORMING PROTECTIVE COATINGS
ON IRON ARTICLES

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This invention relates to a method of forming protective coatings on iron articles and more particularly it relates to an electrochemical method of forming such coatings. As used herein and in the appended claims the term "iron" includes both iron and steel.

Several methods have been proposed heretofore for forming protective coatings on iron objects. Such proposed methods have included painting, plating, and the chemical alteration of the iron surface. While all of these methods provide a certain degree of protection to the iron surface, there are a number of disadvantages inherent in the coatings prepared by these methods. As for example, painting provides a temporary coating. Plating, on the other hand, while being more or less permanent, is rather expensive. As heretofore practiced the formation of coatings by chemically altering the surface of the iron object has been limited in general to the formation of ferrosferric oxide coatings. Such coatings, while being attractive in appearance, are not entirely satisfactory because such surfaces are prone to form fractures, and, as a result, cracks appear in the film and since such an oxide is cathodic to iron, rusting is accelerated. In addition to the disadvantages noted above in regard to painted and plated surfaces, it is generally necessary to refinish the entire surface by repainting or replating if local defects appear in such coatings so as to expose the unprotected metal below.

It is, therefore, a principal object of the present invention to provide a process which obviates the disadvantages of the prior art processes. It is another object of our invention to provide a ferric oxide film that is tough, inert, and non-conductive. It is still another object of this invention to provide a process by which a coating can be formed on the iron surface which can be painted or lacquered thus serving not only to protect the metal against corrosion but also to bond the paint or lacquer to the article. It is yet another object of this invention to provide a process by which a local defect in the protective coating can be repaired without the necessity of reapplying a protective coating to the entire surface. Other objects and advantages of the present invention will become apparent as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention; these are indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In brief, the invention comprises the formation of a protective non-conductive coating of ferric oxide on the surface of an iron object by the anodic oxidation of the latter. This is accomplished by immersing the iron object in an aqueous solution of a non-acidic electrolyte as one electrode. A second electrode, preferably iron or carbon, is immersed in the solution at a distance apart from the first electrode to complete the circuit. A direct current

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of electricity is then passed through the solution wherein the iron object is the cathode and then after a short time the direction of the current flow is reversed making the iron object the anode. During the cathode period the surface of the iron is activated by contact with and by absorption of electrically released hydrogen. When the iron object is the anode a layer of ferrous and ferric hydroxides are formed thereon. After a layer of mixed hydroxides of sufficient thickness is formed the hydroxides are converted to ferric oxide by heating in the presence of air, by treatment with an oxidizing agent, or by a combination of the two.

Almost any water soluble electrolyte may be used in the practice of our invention, provided it will form an aqueous solution the pH of which is not less than 4. Examples of suitable electrolytes are those salts the anion of which include dichromate, halide, nitrate, permanganate, phosphate, and sulfate. The cation portion of said salts include the metals of groups 1 and 2 of the periodic table. Other electrolytes in addition to those listed above may be used including certain iron salts of weak acids as, for example, iron salts of organic acids. Bases such as sodium hydroxide, potassium hydroxide, etc., may be used also. Of the suitable electrolytes, we prefer sodium chloride because of its cheapness and availability. A preferred concentration of the electrolyte ranges from about 0.1 to 1 normal, however, concentrations outside of these limits may be used. An important feature of our process is that ordinary sea water may be used as the electrolyte solution. This makes it possible to form a protective coating on the iron hull of a ship without the necessity of placing the ship in dry dock. The preferred electrolytic E. M. F. is in the range of 1 to 10 volts, but variations above and below these values may be used. As to the current density, that may be varied within rather wide limits as, for example, 0.1 to 1 ampere per square inch based on the surface area of the iron object immersed in the electrolyte solution. A convenient current density is approximately 0.5 ampere per square inch. In reference to the temperature, the solution temperature may vary from any temperature above the freezing point of the electrolyte solution to just below its boiling point. For convenience, we prefer to operate within a range of about 50 to 90° F.

The thickness of the coating produced can be varied by varying either the time of treatment or the current density. As an example, when a current density of 0.1 ampere per square inch is used a coating of sufficient thickness to serve alone as the finish on the surface of the iron object will be produced in about 5 minutes. Obviously, less time will be required to form a thin coating suitable for painting.

The electrode polarity practice is critical, the essential feature being that the cathode is used for a chemical reaction purpose. This result may be produced by direct or by intermittent cathode action, the cycle being cathode on and then power off until film formation is satisfactory. The preferred method is to use an alternating cathodic-anodic time cycle wherein the ratio is equal to 3:2; that is, it is necessary to have a preponderance of cathode time. It is necessary to develop a desirable reaction state of the cathode during the activation period and then develop the mixed hydroxides by the anodic cycle. For practical purposes best results are obtained when the cathodic periods are at least substantial fractions of a second or more. As the length of the cathodic period becomes shorter, to below about one second, the cathodic-anodic time cycle becomes more of greater significance.

As mentioned above after a layer of hydroxides of the desired thickness is formed the hydroxides are converted to the oxide by heat treatment in air and/or by

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treatment with an oxidizing agent. If heat is used, the temperature should not exceed 200° C., the preferred temperature range varying from about 25 to about 100° C. Oxidizing agents suitable for converting the hydroxides to the oxide are those which supply oxygen including oxygen, gases containing free oxygen, hydrogen peroxide, ozone, etc. Generally it is more convenient to first remove the iron object from the electrolytic bath and then convert the hydroxides to the oxide. In some cases it may be desirable to convert the hydroxides to the oxide while the iron object remains in the solution. An example of the latter is the treatment of a ship. The hydroxides may be converted to the oxide while the iron object remains in the electrolytic solution by bubbling air or a gas containing free oxygen through the solution after turning off the current. The hydroxides may be converted to the oxide under the same conditions by directing a stream of hydrogen peroxide on the surface of the iron object.

The ferric oxide films formed by the process of our invention are tough, non-conductive, smooth, and highly resistant to corrosion. In addition this oxide film is absorptive and as a result it can be colored by dyes for decorative purposes. The color penetrates the oxide coating throughout its depth and is not easily removed except by something that removes the coating itself. A preferred method of coloring the coating is to apply the dye to the coating of mixed hydroxides after which the hydroxides are converted to the oxide.

There are many applications for the ferric oxide films of our invention. To mention a few, gun barrels and other gun parts may be protected with such a film that has been dyed black or other dark color which not only affords a great deal of protection but is attractive as well. An automobile body and frame may be "undercoated" by forming a film thereon. In short, about any iron object, the surface of which is subjected to corrosion, may be treated by our process for protection against such corrosion.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given.

Example 1

A piece of sheet iron was polished and then immersed in a 3 percent aqueous sodium chloride solution contained in a glass-lined tank, the temperature and pH of the solution being 76° F. and 10, respectively the latter adjusted to that value by the addition of sodium hydroxide, as one electrode. A carbon rod immersed in the same solution formed the second electrode. An E. M. F. of 5 volts was then applied to the two electrodes, resulting in a flow of current equal to a current density of 0.8 ampere per square inch. The direction of the current flow was such that the sheet iron was first the cathode for a period of 3 seconds, then the flow of current was reversed making the iron the anode for a period of 2 seconds. The current flow was reversed cyclically for a total period of 5 minutes in which the iron was the cathode for 3 seconds and then the anode for 2 seconds. At the end of the 5 minutes a thick coating of ferrous and ferric hydroxides was formed on the surface of the sheet iron. The sheet iron was removed from the sodium chloride solution and placed in an oven for a period of 1 minute at 100° C. which converted the hydroxides to ferric oxide. The ferric oxide film was smooth, tough, and light brown in color, non-conductive and was unaffected by oxygen saturated water containing 3 percent sodium chloride.

Example 2

The procedure of Example 1 was repeated with the exceptions that a current density of .6 ampere per square inch was used and the pH of the electrolyte solution was adjusted to 7 using hydrochloric acid. The ferric oxide

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film obtained was similar to that obtained in Example 1 and exhibited the same resistance to a sodium chloride solution saturated with oxygen.

Example 3

The procedure of Example 2 was repeated with the exception that a 3 percent sodium sulfate solution was substituted for the 3 percent sodium chloride solution. As in Example 1 the ferric oxide film obtained was smooth, tough, and light brown in color and was unaffected by oxygen saturated water containing 3 percent sodium chloride.

Example 4

In this example a 3 percent potassium bromide solution was substituted for the 3 percent sodium chloride solution of Example 2, otherwise the procedure was the same. The ferric oxide film obtained was similar to the films obtained in the preceding examples and showed the same resistance to oxygen saturated water solution of sodium chloride.

Example 5

The procedure of Example 2 was repeated with the exception that a 3 percent solution of sodium hydroxide was substituted for the 3 percent sodium chloride solution. The pH of this solution was 14. The film of ferric oxide formed was smooth, tough, and golden in color. In contrast to the films produced in the preceding examples, this film was electrically conductive.

Example 6

The process of Example 2 was repeated with the exception that a 3 percent lithium nitrate solution was substituted for the 3 percent sodium chloride solution. The film of ferric oxide formed was smooth, tough, and golden in color. As in Example 5, this film was also electrically conductive.

Example 7

In this example a 3 percent potassium dichromate solution was substituted for the 3 percent sodium chloride solution of Example 2, otherwise the procedure was the same as that described in Example 2. The film of ferric oxide formed was similar to that obtained in Example 6.

Example 8

In this example a 3 percent hydrochloric acid solution was substituted for the 3 percent sodium chloride solution of Example 2, otherwise the procedure was the same as that given in Example 2. An unsatisfactory coating was obtained in this example.

Example 9

Examples 3, 4, and 6 were repeated with the exception that the pH was adjusted to 11 rather than 7, by the addition of sodium hydroxide. Example 5 was repeated with the exception that the pH was adjusted to 11 rather than 14 by the addition of hydrochloric acid. In this example the coatings obtained were for all practical purposes identical to the coating formed with a pH of 7.

It was noted that when sodium hydroxide was used the film of ferric oxide could be produced either as a green or a golden color coating depending upon the time of operation. If the current was allowed to flow through the solution for a period of 5 minutes, the coating produced was green in color whereas if 10 minutes were used the coating produced was a golden color.

Example 10

In this example pH effects were studied. A 3 percent sodium chloride solution was made up and the pH thereof adjusted over a range varying from 2 to 12 using either hydrochloric acid or sodium hydroxide to obtain the desired pH. In all cases, coatings were produced on the iron; however, at a pH of 4 or below the coatings were

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unsatisfactory in that they were non-uniform. This example also demonstrated that the most desirable pH range varied within the range of 7 to 11.5.

Example 11

In this example an attempt was made to prepare a film in which the piece of sheet iron was maintained as the anode throughout the entire procedure. The electrolyte used was a 3 percent sodium chloride solution and the current density used ranged from .1 to 36 milliamps per square inch. It was impossible to obtain a film by this process and the material which tended to form on the piece of sheet iron was non-adherent and fell to the bottom of the cell. For that reason a higher current density was not used.

Example 12

In this example the process of Example 11 was repeated with the exceptions that a 3 percent sodium sulfate solution was substituted for the 3 percent sodium chloride solution and the sheet iron was made the cathode throughout the entire run. The procedure was unsuccessful in that no coating at all was obtained.

Example 13

Examples 2, 3, 5, and 7 were repeated with the exception that the layer of mixed hydroxides was converted to ferric oxide by washing the piece of sheet iron with water and then immersing it in a 10 percent hydrogen peroxide solution for a period of 5 seconds followed by washing and drying in air rather than by the heat treatment. The ferric oxide films so produced were similar in all respects to the films produced by heating in the oven at 100° C. for one minute. As in Examples 5 and 7 the sodium hydroxide and potassium dichromate solution produced a film golden in color.

Example 14

Examples 4 and 6 were repeated with the exception that the layer of mixed hydroxides was converted to ferric oxide by washing the piece of sheet iron with water and then immersing it in a 3 percent hydrogen peroxide solution for a period of 5 seconds followed by washing and drying in air rather than by the heat treatment. The ferric oxide films so produced were similar in all respects to the films produced by heating in the oven at 100° C. for one minute. As in Example 6 the use of lithium nitrate produced a film golden in color.

Example 15

Example 1 was repeated with the exception that the layer of mixed hydroxides was converted to ferric oxide by bubbling air enriched with oxygen through the sodium chloride solution for a period of 15 minutes rather than by the heat treatment. The film of ferric oxide so produced was similar in all respects to that obtained by the heat treatment of Example 1.

Example 16

Example 15 was repeated except that ozone was bubbled through the sodium chloride solution rather than air enriched with oxygen. The mixed hydroxides were converted to a film of ferric oxide in less than 3 minutes which was similar in all respects to that obtained by the heat treatment of Example 1.

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The foregoing examples illustrate that the important feature in the preparation of coatings of this invention is the reversal of the direction of the electric current flow whereby the polarity of the iron object is alternately the cathode and then the anode. As to the electrolyte used, that may be selected from a large list either oxidizing or non-oxidizing; however, the pH of the resulting solution should be within the range of about 4 to 12.

It is apparent that many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. The examples given are by way of illustration only and the invention is limited only by the terms of the appended claims.

15 We claim:

1. The process of forming a protective coating on an iron object which comprises immersing said iron object as one electrode in an aqueous solution of an electrolyte the pH of which is not less than four and wherein the cations of said electrolyte are selected from groups 1 and 2 of the periodic table having specific gravities of less than four, immersing another conductor in said solution as a second electrode at a distance apart from said first-mentioned electrode, connecting said electrodes to a source of direct current such that said first-mentioned electrode is negative and said second electrode is positive, allowing a direct current to flow between said electrodes for a period of time until the surface of said first-mentioned electrode is activated by electrically released hydrogen, reversing the polarity of said electrodes until a layer composed of ferrous and ferric hydroxides is formed on said iron object and cyclically repeating said process whereby said iron object is first made cathode and then anode at least once and then converting the said layer of mixed hydroxides to ferric oxide, wherein the cathode-anode time ratio in respect to the iron object is about 3:2.

2. The process of claim 1 wherein the anion of the electrolyte is a sulfate.

3. The process of claim 1 wherein the anion of the electrolyte is a dichromate.

4. The process of claim 1 wherein the anion of the electrolyte is a nitrate.

5. The process of claim 1 wherein the anion of the electrolyte is a hydroxide.

6. The process of claim 1 wherein the pH of the electrolyte solution varies from about 4 to about 12.

7. The process of claim 1 wherein the current density varies from about 0.1 to about 1 ampere per square inch based on the surface of the iron object immersed in the electrolyte solution.

8. The process of claim 1 wherein the electrolytic E. M. F. varies from 1 to 10 volts.

9. The process of claim 1 wherein the concentration of the electrolyte varies from about 0.1 to 1 normal.

10. The process of claim 1 wherein the electrolyte is sodium chloride.

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