

1

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## ELECTRODEPOSITION METHOD

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The present invention relates generally to the art of corrosion inhibition and protective coatings as applied to metal articles and is more particularly concerned with a novel method of covering articles of certain metals with corrosion resistant coatings, and with a novel anode for use in the electrodeposition of protective coatings on the metal articles.

The problem of inhibiting the corrosion of articles having surface portions of ferrous metal, copper, nickel or tin, and the related problem of providing paint, enamel or lithographic coats of good adherence on such metal surfaces are of long-standing in the art and, to the best of our knowledge, neither of these problems has hitherto been satisfactorily solved. The matter of cost has always been a major drawback of anti-corrosion coating operations. When coating mixture or solution strength has been reduced, the resulting materials economy has been substantially completely offset due to the increased time necessary to produce the required coating results. Also, in certain instances diluted coating compositions are not sufficient to produce in a single application the desired corrosion-inhibition or coating adherence-promoting properties that stronger, more expensive compositions can provide on one contact. Thus, both time and manufacturing operations are multiplied by this practice to substantial economic disadvantage.

The foregoing shortcomings and difficulties may largely be overcome and substantially eliminated by virtue of the present invention which affords a substantially more satisfactory and commercial method than heretofore known. The present method enables one to produce a single protective coat on a metal surface which will provide all the corrosion-resistant and coating adherence-promoting characteristics normally desired. Moreover, this result may be accomplished in from  $\frac{1}{10}$  to  $\frac{1}{100}$  of the time required in accordance with the best prior art practice and it does not involve the use of compositions or solutions which are any more expensive than those of the far slower prior art processes. The net result of this invention economically speaking, therefore, is quite surprising and was not heretofore predicted and, in fact, is not predictable from the data and results obtained by others skilled in the art.

Still further, there is no offsetting disadvantage in this process of our invention and as regards certain well-regarded prior art processes, it possesses still another significant advantage in that it may be used without material modification as to the constituents used, the time, cur-

2

rent density or other important factors, regardless of whether the metal surface being treated is of iron, steel, nickel, tin, copper or alloys of these various metals.

In addition to all the foregoing advantages, this invention affords other important advantages through the provision, as indicated above, of a unique anode for use in electrodeposition processes of the present type. This anode does not tend to polarize in use to nearly the extent that ordinary commercial anodes presently generally used polarize. Moreover, by using this anode a substantially uniform higher current is obtained at lower voltage levels than heretofore. The net result of these features is that processes in which this anode is employed are very materially accelerated.

Broadly, the method of this invention comprises the steps of contacting a metal article to be coated with a liquid body of certain critical constituency, contacting a body consisting essentially of lead with said liquid body at a point spaced from the said article to be coated, electrically connecting the lead body and the said article in an electric circuit as an anode and cathode respectively, and then passing an electric current of certain critical density through the said electric circuit and through the liquid body as an electrolyte for a certain critical length of time.

On the basis of the applicants' discoveries on which this process is predicated, the liquid body called for above consists essentially of water and between about 10% and about 35% of chromic acid and between about 3% and about 12% of phosphoric acid. The applicants have further discovered, however, that to achieve best results consistently, the chromic acid and phosphoric acid should be employed in a certain ratio range to each other within the percentage ranges set out above. Thus, in the preferred practice of this invention, the ratio of phosphoric acid to chromic acid will be between approximately 1 to 2 and 1 to 3. Therefore, unlike electrolytes of metal coating processes previously known, the electrolyte of this invention is a highly acid bath which is unbuffered and which contains no salts. Here the contrast is particularly sharp in view of the hitherto general practice of incorporating chromates and dichromates, phosphates, nitrates and various iron, zinc and copper salts in the electrodeposition baths for various purposes.

This liquid body or electrolyte may be prepared in any suitable conventional manner, any substance which would or might have a deleterious effect upon the process or the resulting product being carefully excluded from the resulting aqueous solution. However, preparatory to using this electrolyte, it is preferably brought to a temperature between about 150° F. and 200° F. Satisfactory results may, however, be consistently obtained where the bath is not so preheated but is at approximately room temperature (about 20° C.) when the process is carried out. Because of the interrelation of time and temperature in the method of this invention, the period of bath contact with the article being treated should be longer where the temperature of the bath is lower for the production of generally the same character of corrosion-resistant coatings.

With the liquid body contained in a suitable vessel and

3

with the metal article to be protectively coated and the lead body serving as the anode body immersed in the liquid body and spaced from each other, an electric current of density between about 75 to 500 amperes per square foot of cathode surface is imposed on the system, suitable connections being made to the anode and the said metal article as the cathode. The electric current is flowed through the electrolyte for between about 1 and 20 seconds depending upon the weight of the protective coatings to be applied to the metal article, the thickness of such coatings varying in direct proportion to the length of the electrodeposition period.

The following illustrative, but not limiting, examples of the method of this invention as we have practiced it are offered in further explanation of this invention.

#### EXAMPLE I

In the treatment of a  $\frac{3}{4}$  inch steel conduit to provide a corrosion resistant coating thereon, the conduit was immersed in an aqueous solution containing 23½% chromic acid and 9% of 85% phosphoric acid. The temperature of the solution at the time of immersion was 167° F. An anode consisting of 95% lead and 5% tin was submerged in the solution at the time that the conduit was introduced therein and with the conduit spaced from the anode an electric current of density about 400 amperes per square foot of cathode surface was imposed on the circuit. After 3 seconds of immersion and electric current flow through the aqueous acid electrolyte, the conduit was removed from the electrolyte and subsequently tested to determine its corrosion resistance. The treated outer surface of the conduit test piece proved to be of superior corrosion resistance as indicated by the data set out in Table II hereof in reference to the 3-second test.

#### EXAMPLE II

In a similar test, another test piece of  $\frac{3}{4}$  inch steel conduit was prepared for determination of corrosion resistance qualities by the procedure set forth in Example I using the electrolyte specified therein and maintaining the temperature and current density figures at the level stated therein. The same anode was employed but the immersion time in this case was 5 seconds throughout which period the electric current was continuously passed through the test piece and the electrolyte. The test results compared closely to those set out in Table II in reference to the 5-second test.

#### EXAMPLE III

In a third related experiment, another  $\frac{3}{4}$  inch steel conduit test piece was prepared with a corrosion resistant coating after the manner set out in Example I, the same electrolyte and anode being employed and the electrolyte temperature and electric current density being the same throughout the period. In this case, however, the immersion period was substantially longer, being of 8 seconds duration. The results obtained in corrosion testing the resulting protectively coated outer surface of the conduit test piece compared closely to the results given in Table II for the 8-second item.

#### EXAMPLE IV

Employing the electrolyte described in Example I, the applicability of the method of this invention was tested using a 4 inch by 8 inch sheet panel. The anode employed was that described in Example I and the temperature of the electrolyte was 167° F. throughout the immersion period. The test panel was retained in the electrolyte for 3 seconds with a current density of 325

4

amperes per square foot being maintained throughout that period. The corrosion resistance results obtained are reported in Table II under the third item (the 3-second test).

#### EXAMPLE V

The procedure of Example IV was repeated, using another 4 inch by 8 inch test panel of the same metal stock as employed in Example IV and using the same electrolyte and anode and maintaining the same temperature and current density conditions throughout the immersion period. In this case, however, the sample was submerged in the electrolyte for 5 seconds after which it was removed and tested with the results reported in the fourth item of Table II (the 5-second test).

#### EXAMPLE VI

The procedure of Example IV was repeated again, using the same electrolyte and another 4 inch by 8 inch test panel, the same anode, the same temperature and the same electric density condition throughout the immersion period. However, in this instance, the immersion period was longer, lasting for a total of 8 seconds. The superior corrosion resistance imparted to the sample as a result of this embodiment of the present invention is reflected by the data set out in Table II under the fifth item (the 8-second test).

#### EXAMPLE VII

As one of another series of tests, a sample piece of steel conduit was introduced into an aqueous electrolyte, the temperature of which was between 180° and 185° F. and which contained 25.0% of chromic acid and 8.0% phosphoric acid, the balance consisting of diluent water. A lead anode of the composition described in Example I was employed and the conduit test piece was immersed for a period of 5 seconds in the electrolyte while a current density of 400 amperes per square foot of cathode surface was maintained in the circuit. The resulting article was tested with the results set out in Table I (the 5-second test).

#### EXAMPLE VIII

In an operation similar to the one described above in Example VII, another similar conduit test piece of the same description and composition as that used in Example VII was treated to produce a protective coating, using the electrolyte and anode of Example VII and maintaining the temperature and current density conditions specified in said Example VII. The immersion period, however, was twice as long, i. e., 10 seconds in this case. The resulting article on test showed excellent corrosion resistant characteristics as set out in the 10-second item of Table I hereof.

#### EXAMPLE IX

In still another operation similar to Example VII, a steel conduit test piece of the type used in Examples VII and VIII was provided with a protective coating by means of the procedure set forth in Example VII, the only difference being in the length of the immersion period. In this test, the immersion period was of 15 seconds duration and the corrosion resistance characteristics were highly satisfactory and in line with those set forth under the third item of Table I (the 10-second test).

#### EXAMPLE X

To test this invention on tin-plated surfaces, a test

5

piece bearing a coating of electrolytic tin plate was immersed in an electrolyte consisting of 30% chromic acid and 8.5% phosphoric acid, the balance being water. The electrolyte temperature was between 180° F. and 190° F. during the immersion period which in this case was of only about 3 seconds duration. An anode of the type defined in Example I was employed and a current density of approximately 500 amperes per square foot was maintained throughout the said period. The resulting article showed on test a satisfactory appearance and valuable corrosion resistance characteristics comparable to those set forth in Table I under the 3-second test.

#### EXAMPLE XI

In a parallel test, a similar test piece bearing an electrolytic tin plate coat was immersed in the electrolyte of Example X for a period of 5 seconds, the temperature and current density characteristics being those set forth in Example X and the anode being the same again. The resulting article displayed generally the corrosion resistance characteristics set forth in Table II under the 5-second item and had a satisfactory appearance.

#### EXAMPLE XII

In still another test, an article having a tin plate surface of the type described in Fig. 10 was subjected to the conditions described in Example X, being immersed in the Example X electrolyte at a temperature of about 190° F. with 400 amperes per square foot of cathode surface being applied to the circuit for the entire immersion period which in this case was of 8-seconds duration. The surface of the test piece had a satisfactory appearance on removal from the electrolytic solution and on test showed generally the corrosion resistance characteristics attributed to the 8-second item of Table II.

#### EXAMPLE XIII

A fourth sample piece having an electro-tin plate surface was subjected to the Example X conditions, being immersed in the electrolyte thereof at a temperature of about 170° F. with the current density being maintained for the corrosion resistance period at the level of 400 amperes per square foot of cathode surface. The immersion period in this case was of 10 seconds duration. Superior corrosion resistance characteristics were obtained, the resulting test article showing even better corrosion resistance than the article produced in accordance with the Example XII. Also, the appearance of the surface of this article was completely satisfactory.

#### EXAMPLE XIV

This invention was also tested to determine its applicability to copper surfaces. A test piece of copper sheeting thus was introduced into an electrolyte containing 30% chromic acid and 8.5% phosphoric acid, the balance consisting of water. The temperature of the solution was maintained at 170° F. and an anode of the type used in Example I was employed. A current density of 500 amperes per square foot was imposed upon the circuit throughout the immersion period of 5 seconds duration. The resulting test piece had a surface film displaying the superior corrosion resistance characteristics corresponding to those set out in Table II under the 5-second entry.

#### EXAMPLE XV

In a test paralleling that of Example XIV, a similar test piece of copper sheeting was immersed for 10 seconds in the electrolyte of Example XIV under the current density and temperature conditions specified in that ex-

6

ample. The resulting test piece had a film which displayed superior corrosion resistant characteristics and in fact, was even more resistant to corrosion than the film produced on the test piece of Example XIV.

#### EXAMPLE XVI

In still another test to determine the applicability of this invention to an article having a nickel surface, a nickel sheet test piece was immersed in an electrolyte of the composition described in Example XIV. The electrolyte was at a temperature of 190° F. during the immersion period which was of 10 seconds duration and the current density was maintained at 500 amperes per square foot of cathode surface, the anode employed being of the type described in Example I. The resulting article was tested to determine the corrosion resistance characteristics which proved to be of superior quality comparable favorably with any obtained through the foregoing operations.

To provide a basis for comparison of the processes of the present invention in terms of corrosion resistance characteristics to various types of metal surfaces, a series of tests paralleling those set out above were carried out, employing commercially available preparations. A composition containing chromates, chlorides and complex metal fluorides (known in the trade as Alodine C-5, a product of American Chemical Paint Co. formerly Chromodine #2) was employed in the treatment of stripped conduit, as set forth in Table I. The results of this test are set forth in Table I opposite the Chromodine #2 entry.

In another comparative test, a similar sample of stripped conduit was treated with a solution of the type disclosed in U. S. patent application Serial No. 152,004, filed March 25, 1950, now abandoned in the names of Schofield and Treat and under the title, Zinc Treating Methods and Compositions. Thus the conduit sample was immersed for 5 seconds in a solution at a temperature of about 140° F. consisting essentially of about 6.5 parts of chromic acid, about 3.5 parts of sodium chloride, about 3.5 parts of potassium dichromate and about 85 parts of water. On removal of the conduit sample from this treating solution, it was immediately thoroughly rinsed with a water spray to remove adhering passivating liquor and then permitted to air dry.

In still another comparative test, a sample piece of stripped conduit like those used in the foregoing tests and in certain of the examples set forth above, was immersed in a solution composed of 60 grams per liter of sodium nitrite in water. The immersion period was 10 seconds and removal from the bath was followed with a rinsing and an air-drying operation in that order. This is a standard procedure in the art and the results obtained thereby, as in the case of the above two heretofore commercially employed procedures, were not as satisfactory as any of those obtained in accordance with the present invention and, in fact, were quite inferior to all the other results obtained in this series of tests being inferior even to the blank tests where no protective coating whatever was applied, as set out at the top of Table I.

These comparative tests on Chromodine #2, the solution of application Serial No. 152,004 described above and sodium nitrite were also carried out on unpainted black plate as set forth in Table II. In each instance, however, where the present invention procedure was not used, inferior results were obtained, as Table II clearly shows.

The process of this invention has been carefully compared with prior art methods for providing protective coatings on metal articles in a series of closely controlled experiments. The data collected in the course of these experiments is set forth in tabulated form in the following tables:

Table I

## STRIPPED CONDUIT

| Protective coating application         | Painting system                                                                           | Humidity cabinet test                | Soak test                            | Salt spray test (percent rust)                    | Bake cycle      |
|----------------------------------------|-------------------------------------------------------------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------------------|-----------------|
| None.....                              | Type, urea alkyd; pigment, 37%; vehicle, 63% (non-volatile vehicle, 55%); wt./gal., 8.95. | 10%—Bl, 336 hrs.<br>30%—Bl, 480 hrs. | 10%—Bl, 192 hrs.<br>40%—Bl, 336 hrs. | No adh., 144 hrs.                                 | 30 min. 300° F. |
| Present invention process (5 seconds)  | do.....                                                                                   | O. K., 500 hrs.                      | 5%—Bl, 336 hrs.<br>NFC, 500 hrs.     | O. K., 408 hrs.                                   | Do.             |
| Present invention process (10 seconds) | do.....                                                                                   | do.....                              | 1%—Bl, 240 hrs.<br>NFC, 500 hrs.     | do.....                                           | Do.             |
| Chromodine No. 2.....                  | do.....                                                                                   | do.....                              | O. K., 500 hrs.                      | 1%, 168 hrs.                                      | Do.             |
| Appln. 152,004.....                    | do.....                                                                                   | do.....                              | do.....                              | 1%, 168 hrs.                                      | Do.             |
| Sodium nitrite.....                    | do.....                                                                                   | 100%—Bl, no adh.<br>4 hrs.           | No adh., coating loose, 4 hrs.       | 10%, 408 hrs.<br>20%—Bl, coating rubs off, 4 hrs. | Do.             |

Table II

## UNPAINTED BLACK PLATE

| Protective coating application         | Hours, outdoor exposure (Niles, O.) |          | Total failure | Humidity cabinet (percent rust) | Salt spray (percent rust) |
|----------------------------------------|-------------------------------------|----------|---------------|---------------------------------|---------------------------|
|                                        | 25% rust                            | 50% rust |               |                                 |                           |
| None.....                              |                                     |          | 24<br>840     |                                 |                           |
| Present invention process (1 second)   | 360                                 | 408      | 2,400+        | 20%, 24 hrs.                    | 10%, 24 hrs.              |
| Present invention process (3 seconds)  | 1,048                               | 1,190+   | 2,400+        | 10%, 24 hrs.                    | 5%, 24 hrs.               |
| Present invention process (5 seconds)  | 1,316                               | 2,332    | 3,388         | 10%, 48 hrs.                    | 11%, 48 hrs.              |
| Present invention process (8 seconds)  | 2,428                               |          | 3,316         | 10%, 48 hrs.                    | 19%, 48 hrs.              |
| Present invention process (10 seconds) | 2,760                               | 3,316    |               | 10%, 72 hrs.                    | 10%, 72 hrs.              |
| Chromodine No. 2.....                  |                                     |          |               | 90%, 4 hrs.                     | 90%, 4 hrs.               |
| Appln. 152,004.....                    |                                     |          |               | 80%, 4 hrs.                     | Do.                       |
| Sodium nitrite.....                    |                                     |          |               | 90%, 4 hrs.                     | Do.                       |

NOTE.—In Tables I and II: Adh.=adhesion; Bl=blister; NFC=no further change.

The tests to which the articles prepared in accordance with the foregoing procedures were subjected as indicated in Tables I and II were carried out in essentially the standard accepted manner in every instance. The salt spray tests, for example, were conducted in salt spray cabinets conforming to A. S. T. M. specifications and operated at 95° F. plus or minus 2° F.

The soak test as carried out herein consisted of totally immersing duplicate samples in glass jars filled with diluted water and maintained at 95° F. plus or minus 2° F.

The humidity tests were conducted in a cabinet with approximately 100% relative humidity and maintained at 95° F. plus or minus 2° F.

In evaluating these test results it is apparent on brief consideration of these two tables that the method of this invention is applicable to substantial advantage over prior commercially employed methods on both painted and unpainted metal articles. In every instance in both series of tests, articles prepared in accordance with the present invention are vastly superior in corrosion resistance and/or in paint film adherence to the untreated or blank samples employed to give a basis for comparison of the various methods under study. It is also apparent that no previously known coating method tested proved to be as consistently effective in protecting metal surface as the method of this invention. Furthermore, in most instances, the previously known methods proved to be quite inferior, particularly under the more severe test conditions, both from the standpoint of protecting the surface of the metal body and from the standpoint of keeping the paint film applied to the body tightly adherent thereon.

As indicated above, in the preferred practice of this invention an anode consisting of lead and tin is used although it will be understood that a pure lead anode will serve satisfactorily to produce the present novel metal coating and protecting results. The anode of this invention, is a lead-tin alloy consisting of a major portion of lead and a minor portion of tin. Actually, the lead con-

tent may vary between about 90% and 95%, while the tin content of the anode may vary between about 10% and 5% respectively. The anode, as those skilled in the art will understand, may contain minor amounts of other elements which are not deleterious to the anode, the process in which the anode is to be employed or to the articles with which it is to be associated in an electrodeposition system.

An anode of this type may be made in any suitable conventional manner, as for example, by incorporating molten tin in the required amount in a body of molten lead and casting the resulting liquid alloy into the desired anode form.

By the term "stripped conduit" is meant a steel conduit which is zinc coated and then processed for the removal of the zinc coating by a stripping operation whereby the steel base metal is exposed.

Having thus described the present invention so that others skilled in the art may be able to gain a better understanding and practice the same, I state that what I desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. The method of covering a metal article with a corrosion-resistant coating which comprises the steps of contacting the metal article with a liquid body consisting essentially of water and between about 10% and about 35% chromic acid and between about 3% and about 12% phosphoric acid in the ratio range to each other about two parts and about three parts of chromic acid per part of phosphoric acid, contacting a lead body with said liquid body at a point spaced from said metal article, electrically connecting said lead body and said article in an electric circuit as an anode and a cathode respectively, and passing an electric current of density between about 75 amperes and about 500 amperes per square foot of cathode surface through said electric circuit and through said liquid body as an electrolyte for between about one and about 20 seconds.

2. The method of covering a metal article with a cor-

10. The method of covering a nickel article with a corrosion-resistant coating which comprises the steps of heating to a temperature between about 150° F. and about 200° F. a substantially salt-free liquid body consisting essentially of water and between about 10% and about 35% chromic acid and between about 3% and about 12% phosphoric acid in the ratio to each other between about two parts and about three parts of chromic acid per part of phosphoric acid, immersing the metal article in said liquid body, immersing a lead body in said liquid body at a point spaced from said metal article, electrically connecting said lead body and said article in an electric circuit as an anode and a cathode respectively,

6. The method of covering an iron article with a corrosion-resistant coating which comprises the steps of contacting the metal article with a liquid body consisting essentially of water and between about 10% and about 35% chromic acid and between about 3% and about 12% phosphoric acid in the ratio range to each other between

11

passing an electric circuit of density approximating 100 amperes per square foot of cathode surface through said electric circuit and through said liquid body as an electrolyte for between about one and about 10 seconds, and removing the resulting coated metal from said liquid body.

11. The method of covering a tin article with a corrosion-resistant coating which comprises the steps of contacting the metal article with a liquid body consisting essentially of water and between about 10% and about 35% chromic acid and between about 3% and about 12% phosphoric acid in the ratio range to each other between about two parts and about three parts of chromic acid per part of phosphoric acid, contacting a lead body with said liquid body at a point spaced from said metal article, electrically connecting said lead body and said article in an electric circuit as an anode and a cathode respectively, and passing an electric current of density between about 75 amperes and about 500 amperes per square foot of cathode surface through said electric circuit and through said liquid body as an electrolyte for between about one and about 20 seconds.

12. The method of covering a tin article with a corrosion-resistant coating which comprises the steps of heating to a temperature between about 150° F. and about 200° F. a substantially salt-free liquid body consisting

12

essentially of water and between about 10% and about 35% chromic acid and between about 3% and about 12% phosphoric acid in the ratio to each other between about two parts and about three parts of chromic acid per part of phosphoric acid, immersing the metal article in said liquid body, immersing a lead body in said liquid body at a point spaced from said metal article, electrically connecting said lead body and said article in an electric circuit as an anode and a cathode respectively, passing an electric current of density approximating 100 amperes per square foot of cathode surface through said electric circuit and through said liquid body as an electrolyte for between about one and about 10 seconds, and removing the resulting coated metal from said liquid body.

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