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METHOD OF CATHODICALLY TREATING METALLIC SURFACES

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No Drawing. Filed Jan. 12, 1966, Ser. No. 520,048
15 Claims. (Cl. 204-56)

This application is a continuation-in-part of our copending application Serial No. 178,245, filed March 8, 1962, for Method of Treating Tin Surfaces, now abandoned.

The present invention relates to the treatment of metallic surfaces so as to impart to them improved corrosion-resistance and other desirable properties.

The invention is especially useful in the treatment of blackplate, iron-tin alloy coated ferrous metal bases, and electrolytic tinplate; however, it is also useful in the treatment of hot-dipped tinplate, material vapor-plated with tin, and other tin-containing surfaces such as tin alloys containing, for example, at least 50% tin. By "corrosion" is meant growth of a film of tin oxide on a tin or tin-containing surface, scorch discoloration, rusting of the substrate in the case of blackplate, tinplate or an iron-tin alloy coating on a ferrous base, sulfide staining, etching and the like. Such corrosion is undesirable not only because of appearance and contamination, but also because it reduces the adherence of lacquers, enamels and lithographing inks and causes difficulty during soldering of the material.

Recently, a method has been developed for passivating tin surfaces to inhibit corrosion and especially to retard the formation of tin oxide films on tin surfaces during storage. To this end, the tin-surfaced material is connected cathodically in an aqueous hexavalent chromium electrolyte, in which the chromium is present as chromate or dichromate ions, and an electric current is passed through the material and the electrolyte until chromium is added to the tin surface in an amount sufficient to improve the corrosion resistance of the material. The resulting surface is not corrosion proof but has improved corrosion resistance.

It would not be entirely accurate to say that the surface resulting from this cathodic-chromate treatment is chromium plated. Chromium is added to the surface, perhaps in trivalent form, and probably by a mechanism rather different from conventional plating mechanisms. Although this mechanism is not known with precision, it can be noted that the process is accompanied by the evolution of hydrogen; and it may be that the tin oxide that is inevitably present on the surface of the tin is cathodically reduced by reaction with hydrogen, whereafter it reacts with the chromate to form mixed chromium and tin oxides. The chromium would be trivalent and the tin would probably be tetravalent. Thereafter, the addition of trivalent chromium to the initial layer of tin and chromium oxides might proceed briefly as in a conventional plating process, the trivalent oxide on the surface at the same time interacting with hexavalent chromium remaining in the bath to form mixed chromium oxides on the surface. Suffice it to say, however, that the coating of chromium is a rather complex structure and is therefore presumably adapted to be altered considerably to vary the corrosion resistance it provides.

Accordingly, it is an object of the present invention to provide methods for improving the corrosion resistance of metallic surfaces having cathodically deposited chromium thereon.

Another object of the present invention is the provision of a cathodic-chromate treatment for metallic surfaces which requires a reduced quantity of electrical current to achieve a desired measure of corrosion resistance.

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Still another object of the present invention is the achievement of cathodic-chromate-treated metallic surfaces that require less chromium to achieve a desired degree of corrosion resistance.

Still another object of the present invention is the provision of cathodic-chromate-treated metallic surfaces having better corrosion resistance than was obtainable heretofore.

Finally, it is an object of the present invention to provide a method of treating metallic surfaces that will be simple, easy, inexpensive and reliable to practice.

Other objects and advantages of the present invention will become apparent from a consideration of the following description.

Briefly, the present invention is the discovery that improved corrosion-resistance and other desirable surface characteristics can be imparted to metallic surfaces such as ferrous metal surfaces and material having tin or tin-containing surfaces, by the use of a known cathodic-chromate treatment, if in the electrolyte in which that treatment is practiced there is incorporated in solution a small but effective amount of a substance which in solution is a source of borate ions. Suitable sources of borate ion are boric acid and water soluble borates, it being necessary to observe the limitation in the case of all such borates that the metal cation should be substantially higher in the electromotive series than is chromium to prevent preferential deposition or codeposition of the metallic cation to the exclusion or detriment of the chromium. Boric acid and the alkali metal borates are preferred. Particularly preferred from a standpoint of economy are boric acid, sodium borate, borax and potassium borate. Also operative are lithium borate, strontium borate and zinc borate, but most of these latter compounds are too costly to be economically practical.

The substance which is a source of borate ion can be present over a wide range of concentration, from about 0.1 ounce per gallon of aqueous electrolyte or even less, up to the limit of solubility. The preferred range is usually about 1-5 ounces per gallon of electrolyte. The pH of the electrolyte should be at least 5, and preferably about 5-8, with better results normally being obtained at a pH of about 6.5-7.5.

Apart from the addition of the above substance, the chromate electrolyte and its use may be conventional, except for the fact that the total current needed to impart a given degree of chromate corrosion resistance to the metallic surface is reduced by about half. Thus, the electrolyte bath may contain the usual amounts of hexavalent chromium in the form of a chromate such as sodium dichromate, sodium chromate, chromic acid or other water soluble chromates, in the usual amounts of 1-10 ounces per gallon, preferably about 1-4 ounces per gallon of electrolyte. Chromic acid is preferred. The bath operates at the usual temperature range of about 70° to about 200° F., preferably about 120°-160° F. and more preferably about 150°-160° F. The current density is conventional, that is, about 10-70 amperes per square foot, preferably about 40-50 amperes per square foot. The amount of current to produce an improved deposit according to the invention may be about 6-72 coulombs per square foot of treated surface area, a preferred range being about 12-36 coulombs per square foot, more preferably about 24-36 coulombs per square foot. Best results are usually obtained at about 30 coulombs per square foot. Preferably, the process is operated as a continuous process, in which continuous strip material passes continuously through the electrolyte. As is usual, current density is made to vary directly as the speed of the strip

through the electrolyte. Moreover, as is also conventional, the electrolyte is kept free from phosphate inclusions which otherwise would tend to codeposit with the chromate.

Although the ratio to each other of the newly added substance and the conventional chromate is not critical, the manipulation of this ratio is nevertheless a convenient way to adjust the pH of the electrolyte to a desired range. The pH of the electrolytes of the present invention is not critical; but for each combination of chromate and new additive, there will be a preferred pH range in which optimum chromium deposition will occur. In each case, the preferred pH range can be determined by trial and error. For the preferred chromic acid-borax (sodium borate) system, a pH range of 6.5-7.5 is preferred. As it happens, an aqueous electrolyte containing 3 ounces per gallon of borax with one ounce per gallon of chromic acid will have roughly that pH to begin with, so that the borax need do no more than improve the corrosion resistance of the deposited chromium, and hence need be added in only minimal amounts. In the case of other systems, the added borate or boric acid may be adjusted in concentration to bring the pH of the resulting electrolyte within a desired range, in which case the additive may be used in relatively greater quantities than otherwise would be necessary. In a borax-chromic acid system, a desirable pH range of 6.5 to 7.5 can be maintained by using about 0.75-1.3 moles of borax per mole of chromic acid, that is, about 3-5 ounces per gallon of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) per ounce per gallon of chromic acid in the electrolyte. For the system sodium chromate-boric acid, a desirable pH range of 7.25-7.5 may be maintained by using about 0.4-2.0 moles of sodium chromate per mole of boric acid, that is, about 1.0-5.0 ounces per gallon of sodium chromate per ounce per gallon of boric acid.

The present invention is especially useful in treating ferrous metal substrates, tinplate produced by the hot dip and electrolytic methods, and iron-tin alloy coated ferrous metal bases. Thin gauge cold reduced flat rolled steel products in general, and especially blackplate of tinplate gauge and quality, respond readily to the treatment. A preferred iron-tin alloy coated ferrous metal base for treatment in accordance with the invention may be prepared by applying a thin layer of free tin to clean ferrous metal in an amount of 0.02-0.05 pound per base box (62,720 square inches) and preferably 0.03-0.04 pound per base box, and the layer of free tin is converted substantially completely to an alloy layer by heating at an elevated temperature. The tin coating may be alloyed at a temperature of about 450-650° F., and substantially complete conversion of the free tin to the alloy usually may be obtained within this temperature range by heating for about 1/4 to 1 1/2 seconds. It is understood that the heat treatment at a given temperature is continued until the free tin is converted substantially completely to the iron-tin alloy. In some instances, temperatures higher than 650° F. may be useful, such as temperatures up to about 700-750° F. for controlled and usually short periods of time.

The metallic surfaces treated in accordance with the invention are bright and are not discolored. Also, films containing less than 2,000, and preferably less than 1,000, micrograms of chromium per square foot give as good or better protection than the much heavier films produced by prior art processes. The films produced in accordance with the invention have other unusual and unexpected properties which make the treated product especially useful as a container stock. Containers prepared from the treated product are very corrosion resistant and perform much better than prior art materials in preserving certain foods which are difficult to store, such as vegetarian vegetable soup. There is also less discoloration during side seam soldering of containers prepared from the treated product.

To enable those skilled in this art to practice the invention, the following illustrative examples are given:

Example I

Continuous steel strip of 33 gauge, that is, 0.0090" thickness, having an electroplated coating of tin on both sides thereof to a thickness of a quarter pound per base box, the strip having an average width of about 30", is cathodically connected and is introduced into and passed through an aqueous electrolyte containing 3 ounces per gallon of borax and 1 ounce per gallon of chromic acid in solution. A steel anode is used. The strip is run through the electrolyte at a linear speed of about 1,200 feet per minute and during its passage through the bath is subjected to a total current of 30 coulombs per square foot of strip. The pH stays within the range of 6.8 to 7.3. 600-700 micrograms of chromium per square foot deposit on the strip.

The chromate-treated strip, which is bright and substantially unchanged in appearance, is allowed to stand twenty-four hours under warehouse conditions, so that a thin initial film of tin oxide forms. The strip is then cut into a plurality of small pieces and each is individually connected as a cathode in an electrolyte of 0.001 N hydrobromic acid with a platinum anode. The area of the specimen is measured and the current and time are recorded. The current is maintained constant, and potential is plotted on the ordinate versus time on the abscissa. The initial potential remains rather constant while the initial tin oxide film is undergoing electrolytic removal; but the potential sharply breaks when the oxide film is completely removed. This sharp break marks the duration of the time for oxide film removal and is a good general indication of the extent of oxide film formation. Expressed in terms of millicoulombs equivalent per square inch, the average value for the samples is 2 mce./in.².

A further quantity of the strip is stored for twenty-four hours under conditions designed to accelerate oxide film formation, namely, 65% relative humidity and 185° F. The accelerated material is also cut up into small samples and tested in hydrobromic acid electrolyte of the same composition, whereupon the potentiometric end point of the thicker oxide film removal occurs at 15 mce./in.² average for all tests.

Comparable results are obtained by the use of chromates other than chromic acid, namely, sodium dichromate, or sodium chromate, and by the use of addition agents other than borax (sodium borate), namely, boric acid, lithium borate and potassium borate.

In each case, the tin surfaces according to the present invention have good resistance to scorch discoloration, good lacquer adhesion properties, high resistance to sulfide stain, good soldering properties, and high resistance to other forms of corrosion. The treatment of the invention is especially useful in preventing discoloration during side beam soldering of containers, and also in preventing corrosion of containers for vegetarian vegetable soup.

Example II

Black plate strip of tinplate gauge and quality is passed through a prior art cleaning bath for the removal of grease, dirt and other foreign matter from the strip surface. The clean strip is introduced into and passed through an aqueous electrolyte containing 3 ounces per gallon of borax and one ounce per gallon of chromic acid in solution. A steel anode is used, and the ferrous metal strip is connected as the cathode and treated electrolytically to deposit a chromate-containing film thereon. The strip is run through the electrolyte at a linear speed of about 1200 feet per minute and during the passage through the bath is subjected to a total current of 30 coulombs per square foot of surface area. The pH of the electrolyte is 6.8-7.3 during the run, and 300-400 micrograms of chromium per square foot of strip surface area is deposited.

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Upon subjecting the treated black plate strip to prior art rust and lacquer adhesion tests, the treatment is found to impart a chromium-containing film which gives good resistance to atmospheric corrosion, as well as enhanced corrosion resistance when subjected to other types of corrosion elements. The treatment also imparts good adhesion with respect to lacquer, varnish and the usual protective organic coatings applied on beverage containers.

Example III

The procedure of Example II is repeated with the exception of first electroplating a coating of tin on the cleaned black plate strip in an amount of .03 pound per base box (62,720 sq. in.), followed by alloying the free tin by heating at about 600° F. for approximately one second. The resultant substrate was coated with an iron-tin alloy layer which contained substantially no free or unalloyed tin.

The ferrous metal substrate coated with the iron-tin alloy layer was treated and tested by the procedure of Example II. The treatment produced a film on the surface which gave greatly improved resistance to corrosion, and which also imparted good adhesion with respect to lacquer, varnish and the usual organic coatings normally used for beverage containers.

Example IV

The general procedure of Example I was followed over four runs on the same lot of electrolytic tinplate produced as described in Example I, with the exception of using four different types of electrolyte and treating conditions as follows:

Run 1. An electrolyte and current conditions in accordance with the invention was used in this run. The electrolyte contained 3 ounces per gallon of borax and one ounce per gallon of chromic acid. The pH of the electrolyte was 7.7-7.9, and the tinplate was subjected to a total current of 30 coulombs per square foot of treated area.

Run 2. The electrolyte and current conditions recommended by a prior art procedure was used in this run. The electrolyte contained 100 g./l. of chromic acid and 8 g./l. of boric acid. The pH of the electrolyte was 0.1, and the tinplate strip was subjected to a total current of 640 coulombs per square foot of treated area. These are the lowest concentrations for the electrolyte ingredients, and also the lowest current conditions which were recommended for use in the prior art procedure.

Run 3. Another prior art electrolyte and procedure was tested in this run. The electrolyte contained 100 g./l. of chromic acid, 8 g./l. of boric acid and 7.5 g./l. of glycerine. The pH of the electrolyte was 9.14, and the tinplated strip was subjected to a total current of 640 coulombs per square foot of surface area. These treating conditions likewise represented the lowest concentrations for the ingredients of the electrolyte, and the lowest current conditions, which were recommended by this prior art procedure.

Run 4. This run was conducted using the current conditions of the present invention, but the electrolyte contained glycerine, as in the prior art electrolyte for Run 3. The electrolyte contained 10 g./l. of chromic acid, .1 g./l. of boric acid and .75 g./l. of glycerine. The pH was 2.0, and the tinplated strip was subjected to a total current of 30 coulombs per square foot of treated area.

Samples of the four treated strips produced by the four runs set out above were tested in accordance with the procedure of Example I. In addition, a prior art capillary rise solderability test was performed by placing a sample of tinplate folded back on itself in a solder bath and measuring the capillary rise of the solder. This is the standard solderability test in which a minimum rise of $\frac{5}{16}$ ", with a lot average of $\frac{9}{16}$ ", being required for good container making qualities. The treated strip must pass the capillary rise solderability test in order to be

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satisfactory in the manufacture of containers such as "tin" cans.

The following results were obtained:

TABLE I

Run No.	Initial Oxides, mce./in. ²	Microgram, Cr per sq. foot	Solderability by Cap. Rise, 1/16"	Remarks
1-----	2-3	600-720	9-18	Treated surface bright.
2-----	2-3	14,000-16,000	0	Heavily discolored.
3-----	3-5	7,000-9,000	0	Do.
4-----	3-5	1,850-1,950	0	Do.

It may be observed from the data in Table I that the treatment of the present invention is capable of producing a product which has a bright, treated surface. The appearance of the surface is very important, as the tinplate surface must be left substantially unchanged in appearance in order to be satisfactory as a container stock. Additionally, it is also essential that the container stock pass the solderability test, and only the product of the present invention is capable of doing this. Only the product of the present invention is satisfactory for the manufacture of containers and thus the process of the present invention is unique in its ability to impart greatly improved corrosion resistance without adversely affecting the appearance and solderability properties. Surprisingly, this may be accomplished by using much less current and much lighter chromium-containing films.

A more effective chromate treatment is practiced by the present invention with the use of even less chromium than before, with the result that not only is chromium conserved, but much more importantly, the quantity of electrical current needed to impart a desired degree of corrosion resistance is very greatly reduced. It is not known why this should be so; suffice it to say that such improved results unexpectedly occur.

Although the present invention has been described and illustrated in connection with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit of the invention, as those skilled in this art will readily understand. Such modifications and variations are considered to be within the purview and scope of the present invention as defined by the appended claims.

What is claimed is:

1. A method of treating material having a metallic surface to improve the corrosion resistance of said surface, comprising making the said material a cathode in an aqueous hexavalent chromium electrolyte consisting essentially of about 1-10 ounces per gallon of a water soluble chromate and a small but effective amount not less than about 0.1 ounce per gallon of a substance selected from the class consisting of boric acid and water soluble borates of which the cations will not deposit at the cathode under the process conditions, and adding a chromium-containing film to said surface in an amount sufficient to improve the corrosion resistance of the material by passing an electric current through the material and the electrolyte, the electrolyte having a pH of at least 5 and the said substance being effective to reduce substantially the quantity of current necessary to achieve said corrosion resistance.

2. The method of claim 1 wherein the said chromate is chromic acid, the said substance is sodium borate and the pH of the electrolyte is about 5-8.

3. The method of claim 1 wherein the quantity of electric current is about 6-72 coulombs per square foot of the treated surface area of the material.

4. The method of claim 1 wherein the said chromate is chromic acid, the said substance is sodium borate, the pH of the electrolyte is 5-8, and the quantity of electric

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current is about 6-72 coulombs per square foot of the treated surface area of the material.

5. The method of claim 1 wherein the said material having a metallic surface is iron-tin alloy coated ferrous metal.

6. The method of claim 5 wherein the electrolyte contains chromic acid as the said chromate and sodium borate as the said substance, the pH of the electrolyte is about 5-8, and the quantity of electric current is about 6-72 coulombs per square foot of the treated surface area of the iron-tin alloy coated ferrous metal.

7. The method of claim 6 wherein the quantity of electric current is about 24-36 coulombs per square foot of the treated surface area of the iron-tin alloy coated ferrous metal and the pH of the electrolyte is about 6.5-7.5.

8. The method of claim 1 wherein the said material having a metallic surface is tinplated ferrous metal.

9. The method of claim 8 wherein the electrolyte has a pH of about 5-8 and chromic acid as the said chromate and sodium borate as the said substance.

10. The method of claim 8 wherein the quantity of electric current is about 6-72 coulombs per square foot based on the treated surface area of the tinplated ferrous metal.

11. The method of claim 8 wherein the pH of the electrolyte is about 6.5-7.5, the electrolyte contains chromic acid as the said chromate and sodium borate as the said substance, and the quantity of electric current

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is about 24-36 coulombs per square foot based on the treated surface area of the tinplated ferrous metal.

12. The method of claim 11 wherein the quantity of electric current is about 30 coulombs per square foot based on the treated surface area of the tinplated ferrous metal.

13. The method of claim 1 wherein the said material has a ferrous metal surface.

14. The method of claim 13 wherein the electrolyte contains chromic acid as the said chromate and sodium borate as the said substance, the pH of the electrolyte is about 5-8, and the quantity of electric current is about 6-72 coulombs per square foot of the treated area of the ferrous metal surface.

15. The method of claim 14 wherein the quantity of electric current is about 24-36 coulombs per square foot of the treated area of the ferrous metal surface and the pH of the electrolyte is about 6.5-7.5.

References Cited by the Examiner

UNITED STATES PATENTS

2,733,199	1/1956	Wick	204-56
2,780,592	2/1957	Wick et al.	204-56

FOREIGN PATENTS

863,234	3/1961	Great Britain.
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