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METHOD OF TREATING TIN-CONTAINING SURFACES

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

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

The invention is especially useful in the treatment of electrolytic tin plate and iron-tin alloy coated ferrous metal bases; however, it is also useful in the treatment of hot-dipped tin plate, 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 or metal oxide on the tin or tin-containing surface, scorch discoloration, rusting of the substrate in the case of tin plate or an iron-tin alloy coating on a ferrous base, sulfide staining, etching and the like. Such corrosion is undersirable not only because of appearance and contamination, but also because it reduces the adherence of lacquers, enamels and lithographing inks and cause diffculty 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 chrominum 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 in 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 intial 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 chrominum 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 a method of improving the corrosion resistance of tin-containing surfaces in general, and especially tin plate and iron-tin alloy coated ferrous metal bases, having cathodically deposited chromium thereon.

Another object of the present invention is the provision of a cathodic-chromate treatment requiring a reduced

quantity of electrical current to achieve a desired measure of corrosion resistance.

Still another object of the present invention is the achievement of cathodic chromate-treated tin and tin-containing 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 tin and tin-containing surfaces having better corrosion resistance than was obtainable heretofore.

Finally, it is an object of the present invention to provide a method of treating tin and tin-containing 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 material having a tin or tin-containing surface, 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 acetate ions. Suitable sources of acetate ion are acetic acid and water soluble acetates, it being necessary to observe the limitation in the case of all such acetates 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 of detriment of the chromium. Acetic acid and the alkali metal acetates are preferred. Particularly preferred from a standpoint of economy are acetic acid, soduim acetate, potassium acetate and calcium acetate. Also operative are lithium acetate, barium acetate, strontium acetate, magnesium acetate, aluminum acetate, manganese acetate and zinc acetate, but most of these latter compounds are too costly to be economically practical.

The substance which is a source of acetate 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 about 0.3–0.5 ounce per gallon of electrolyte. From about 0.1 to below about 0.3, improved results are obtained which are not as good as in the preferred range. Above the preferred range, on substantial improvement in the results is obtained such as would justify the cost of higher concentration of the substance. Accordingly, an amount above about 0.5 ounce per gallon is merely wasteful except as will be hereinafter noted.

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 tin or tin-containing 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 2–4 ounces per gallon of electrolyte. Sodium dichromate 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 from about 6 coulombs per square foot up, a preferred range being about 12–36 coulombs per square foot, more preferably about 18–30 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 sodium dichromate-sodium acetate system, a pH range of 5.0–5.3 is preferred. As it happens, an aqueous electrolyte containing 3 ounces per gallon of sodium dichromate will have roughly that pH to begin with, so that the sodium acetate need do no more than improve the corrosion resistance of the deposited chromium, and hence need be added in only minimal amounts. But in the case of less preferred systems, the added acetate or acetic acid can also be used to bring the pH within a desired range, in which case the additive will be used in relatively greater quantities. For example, the system sodium chromate-acetic acid can be maintained at a desirable pH range of 6.0–6.5 by using 1.2–2.0 moles of sodium chromate per mole of acetic acid, that is, 3.0 to 5.5 ounces per gallon of sodium chromate per ounce per gallon of acetic acid. A sodium acetate-chromic acid electrolyte can be maintained at a desirable pH of 4.1 to 4.8 by the use of 1.2–2.0 moles of sodium acetate per mole of chromic acid, that is, 1.7–2.7 ounces per gallon of sodium acetate per ounce per gallon of chromic acid. These latter examples are among the aforementioned exceptions to the rule that use of the additive above about 0.5 ounce per gallon is merely wasteful.

The present invention is especially useful in treating tinplated ferrous metal produced by the electrolytic and hot dip methods, and iron-tin alloy coated ferrous metal bases. When preparing a preferred irontin alloy coated ferrous metal base, a clean ferrous metal such as blackplate is coated with a thin layer of free tin 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 ¼ to 1½ 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.

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

Example 1

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 0.3 ounce per gallon of sodium acetate and 3.5 ounces per gallon of sodium dichromate in solution. A steel anode is used. The strip is run through the electrolyte at a linear speed of about 1200 feet per minute and during its passage through the bath is subjected to a total current of 6 coulombs per square foot of strip. The pH stays within the range 5.0 to 5.3. 156 micrograms of chromium per square foot deposit on the strip.

The chromate-treated strip 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 sqare inch, the average value for the samples is 9.5 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 28.2 mce./in.^{2} average for all tests.

Example 2

Example 1 is repeated, except that the sodium acetate is omitted. 200 micrograms of chromium per square foot are deposited, which after twenty-four hours storage results in initial oxide film removal at 11.2 mce./in.^{2} and accelerated oxide film removal at 27.5 mce./in.^{2}.

Example 3

Example 1 is repeated, except that the traveling strip is subjected to 12 coulombs per square foot. 196 micrograms of chromium per square foot are deposited, initial oxide film thereafter disappearing upon the application of 6.5 mce./in.^{2} and the accelerated oxide film disappearing upon the application of 17.3 mce./in.^{2}.

Example 4

Example 2 is repeated, but with the 12 coulombs per square foot total current of Example 3. 286 micrograms of chromium per square foot are deposited, the initial oxide film disappearing upon the application of 8.5 mce./in.^{2} and the accelerated oxide film disappearing upon the application of 18.3 mce./in.^{2}.

Examples 5–8

Examples 1–4 show the pattern of the experiments by which the effectiveness of the electrolyte is tested with and without an addition agent of the present invention and with progressively increasing total current. The remaining examples can therefore be set forth in tabular form without a detailed explanation. The following table lists the remaining examples and also the first four examples, for purposes of easy comparison:

TABLE 1

Example	Na Acetate Addition Agent	Total Current Coulombs per ft.^{2}	Chromium Deposited per ft.^{2}	Initial Oxide, Film, mce./ft.^{2}	Accelerated Oxide Film, mce./ft.^{2}
1	yes	6	156	9.5	28.2
2	no	6	200	11.2	27.5
3	yes	12	196	6.5	17.3
4	no	12	286	8.5	18.3
5	yes	18	343	4.3	10.0
6	no	18	360	7.5	17.2
7	yes	30	380	4.3	9.0
8	no	30	394	6.2	13.7

Comparable results are obtained by the use of chromates other than sodium dichromate, namely, chromic acid or

sodium chromate, and by the use of addition agents other than sodium acetate, namely, acetic acid, lithium acetate, potassium acetate, and calcium acetate.

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.

In particular, it will be noted from Table 1 that at 6 coulombs per square foot, there is not a great deal of difference between the tin oxide film-forming properties of the surfaces with or without the addition agent of the present invention, but that substantially less chromium is deposited when the present invention is practiced. This is a useful result as it conserves the chromate reagent. At about 12 coulombs per square foot, the chromate deposit is still substantially less when the present invention is practiced than when it is not; and in addition, the quantity of tin oxide that forms upon storage begins to drop off noticeably. By 18 coulombs per square foot, it remains true that less chromium is deposited, but the remarkable feature of the invention in this current range is that markedly less oxide forms. At 30 coulombs per square foot, less chromium is used but the amount of oxide formation remains very substantially less than when the invention is not practiced.

Thus, 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.

Example 9

An iron-tin alloy coated steel strip is prepared by electroplating about 0.03 pound per base box of tin on cleaned black plate strip, followed by heating the tin coating at 500–600° F. for one second to completely alloy the tin with the iron. The resulting surface of the strip is uniformly coated with an iron-tin alloy layer and has substantially no tin in the free or unalloyed state.

The above prepared iron-tin alloy coated steel strip is treated to improve the corrosion resistance by the procedures of Examples 1–8, and comparable results are obtained.

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 tin-containing surface to improve the corrosion resistance of said surface, comprising making the 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 acetic acid and water soluble acetates of which the cations will not deposit at the cathode under the process conditions, and passing an electric current through the material and the electrolyte until a chromium-containing film is added to said surface in an amount sufficient to improve the corrosion resistance of the material, 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 present in the electrolyte in an amount of about 2–4 ounces per gallon.

3. The method of claim 1 wherein the quantity of electric current is about 12–36 coulombs per square foot of the treated surface area of the material.

4. The method of claim 1 wherein the said chromate is present in the electrolyte in an amount of about 2–4 ounces per gallon and the quantity of electric current is about 12–36 coulombs per square foot of the treated surface area of the material.

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

6. The method of claim 5 wherein the said electrolyte contains about 2–4 ounces per gallon of sodium dichromate and about 0.3–0.5 ounce per gallon of sodium acetate.

7. The method of claim 6 wherein the quantity of electric current is about 12–36 coulombs per square foot of the treated surface area of the material.

8. The method of claim 1 wherein the said material having a tin-containing surface is tin-plated ferrous metal.

9. The method of claim 8 wherein the said electrolyte contains about 2–4 ounces per gallon of sodium dichromate and about 0.3–0.5 ounce per gallon of sodium aceate.

10. The method of claim 8 wherein the quantity of electric current is about 12–36 coulombs per square foot based on the treated surface area of the material.

11. The method of claim 8 wherein the pH value of the electrolyte is about 5 and the quantity of electric current is about 18–30 coulombs per square foot based on the treated surface area of the material.

12. The method of claim 8 wherein the electrolyte contains about 3 ounces per gallon of sodium dichromate and has a pH value of about 5, and the quantity of electric current is about 24 coulombs per square foot based on the treated surface area of the material.

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