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3,532,608

**METHOD OF TREATING STEEL AND  
ELECTROLYTE THEREFOR**

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9 Claims

**ABSTRACT OF THE DISCLOSURE**

This invention relates to a process for electro depositing a layer of metallic chromium and an adherent, overlying chromium-containing oxide film. The sheet is cathodically coated at 25 to 300 amps/ft.<sup>2</sup> in an electrolyte containing 5 to 80 g./l. of chromium trioxide and 0.25 to 5 g./l. of either cobaltous chloride or sulfamic acid. Adherence of the overlying oxide film is enhanced by an initial anodic treatment in a similar electrolyte.

**BACKGROUND OF THE INVENTION**

Flat-rolled steel has long been produced with an overlying layer of tin, either applied by hot dipping or, more recently, by electrodeposition. The tin layer serves as a protective, corrosion-resistant coating of particular value when the thus-coated steel is used in the manufacture of food and beverage cans and other containers requiring a corrosion-resistant surface. The tin layer also facilitates soldering of the side seam construction usually employed in the manufacture of such articles.

More recently, such containers have been produced by welding or by adhesive bonding of the side seam, thus enabling elimination of the tin layer required for effective soldering. Elimination of the costly tin layer is, of course, of considerable economic advantage.

Untinned flat rolled steel stock, when used for can-making purposes, must be provided with a protective coating, as enamel, lacquer and the like, to prevent deleterious chemical reaction between corrosive can contents and the metal can body. Such protective coatings are most frequently of a variety of compositions, being specific in nature and function to the intended application of the coated container, and are preferably applied to the flat metal container stock by the container manufacturer, rather than by the steel producer.

Since the uncoated flat-rolled steel is susceptible to rusting during extended periods of shipment and storage, and since rusting detracts from the desired clean, bright appearance of the steel and also deleteriously affects adherence of subsequently applied protective coatings, it is essential that rusting be prevented and the steel delivered to the container manufacturer in a suitable condition for application and retention of the necessary protective coatings even after considerable periods of storage under humid conditions. Further, since the latter coatings are generally transparent, any treatment of the steel by the

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steel producer must not detract from the desired bright metallic appearance of the finished fabricated article.

Additionally, it is necessary that the metal stock provided to the can manufacturer be of such a nature as to resist delamination of the subsequently applied enamel or lacquer coating during fabrication, and also that the stock resist undercutting of such overlying protective coating by corrosive action of the can contents at the sites of defects in the enamel or lacquer coating or breaks, cuts or other defects caused during container fabrication.

Still further, in the case of containers having an adhesively bonded lapped side seam, it is required by the container manufacturer that such bond have a minimum peel (separation) strength of 25 pounds per inch of seam width for steel stock of 55 to 60 pounds basis weight (about 6 to 7 mils thickness).

Ordinary, untreated, cleaned and oiled flat-rolled steel (black plate) does not satisfy all of the foregoing requirements.

Most recently, tin-free steels have been made available for container manufacture and which provide, on the flat-rolled steel surface, either a thin layer of electrolytically deposited metallic chromium (for example, Uchida et al. U.S. Pat. No. 3,113,845), a film of chromium-containing oxides (for example, Kitamura U.S. Pat. No. 2,998,361), or both (for example, Yonezaki et al. U.S. Pat. No. 3,296,100).

However, electroplating processes are inherently costly and, for their successful use in production of stock for container manufacture, it is necessary that such electrolytic treatments add only insignificantly to the cost of production of untreated black plate.

Specifically, such electrolytic processes, to be of maximum commercial utility and value, must meet the following economic criteria:

- (1) the cost of the electrolytic bath chemicals must be low;
- (2) the concentration of the bath chemicals must be low in order to avoid economic loss due to high dragout losses at the required high line speeds, e.g. 500 to 1500 feet per minute or greater;
- (3) the bath treating time must be low, in order to reduce to an economically feasible number, the treating tanks required;
- (4) the power requirements must be low;
- (5) the bath composition must be uncomplicated in preparation, control and maintenance;
- (6) the process must be sufficiently flexible in operation, so that only minor changes in process conditions can be made to produce a wide range of products of optimum characteristics for many end-use applications; and
- (7) the overall process must be susceptible of easy and accurate control to insure optimum product quality without excessive post-production and prefabrication quality testing.

The prior art, such as that referred to above, does not provide processes having all of the foregoing desirable attributes and which also provide products having all of the aforementioned desirable property characteristics. For example, although U.S. Pat. No. 3,296,100 teaches the production of articles comprising a steel base, as flat-

rolled can stock steel, provided with an intermediate, thin metallic chromium layer and an overlying chromium oxide film, by a process using a low concentration (10–50 g./l.) of chromic acid plus a sulfuric acid radical catalyst, a pre-treatment of the bath by electrolysis is taught as required to provide a certain proportion of trivalent chromium ions in the bath solution. U.S. Pat. No. 3,113,845 teaches production of a thin metallic chromium layer on steel, such as can stock, by means of an electrolytic bath wherein the chromic acid content, as is usual in most prior art chromium plating baths, is relatively high 100–250 g./l. U.S. Pat. No. 2,998,361 teaches the production of hydrated chromium oxide films only, the formation of such films being promoted by the use of aromatic sulfonic acids and sulfonates, in a chromic acid-containing electrochemical bath.

Chromium deposition, in thin layers on can stock steel, has also been effected from electrochemical baths containing, as the metallic chromium-depositing promoter or catalyst, phosphoric acid, boric acid and oxalic acid (U.S. Pat. No. 3,032,487). The necessity of boiling the oxalic acid-containing bath until oxidation of the latter compound is complete, is a further illustration of a costly, time-consuming procedure which detracts from the commercial value of prior art processes.

Expensive and hard to handle fluorine-containing compounds, as hydrofluoric acid, silicofluoric acid and the like, have also been used in the prior art, in conjunction with usual metallic chromium-depositing catalysts, such as sulfuric acid and sulfates, to promote production of bright chromium plate.

#### SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a new and improved, electrochemically treated, tin-free, flat-rolled steel product which satisfies all of the foregoing requirements for container manufacture.

It is another object of the invention to provide a new and improved, low cost, readily controllable, electrolytic process for the production of a wide range of treated, flat-rolled steel products having on the surfaces thereof controlled-thickness layers of metallic chromium and chromium-containing oxides.

It is a further object to provide a new and improved low-cost electrolytic bath for use in the inventive process and in the production of the products of the invention.

In accordance with the foregoing objects, a preferred embodiment of the invention comprises an aqueous chromium plating bath containing from about 15 to about 25 grams per liter (g./l.) of chromium trioxide ( $\text{CrO}_3$ ), and from about 0.25 to about 1.0 g./l. of cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), or from about 0.25 to about 2.0 (g./l.) of sulfamic acid ( $\text{H}_2\text{NSO}_3\text{H}$ ).

By maintaining such a bath at a temperature of from about 70° to about 190° F., and passing continuously therethrough a cleaned carbon steel strip, as cathode, for a time from about 0.25 second to about 10 seconds, at a cathodic current density of from about 25 to about 300 amperes per square foot (a.s.f.), with application to the cathode of from about 50 to about 1000 coulombs per square foot (coulombs/ft.<sup>2</sup>) of electrical energy, there is provided a treated steel strip product having on the surface thereof a double-layered protective coating comprising a layer of metallic chromium adherent to the steel surface, and, overlying the chromium layer, a film of hydrated, chromium-containing oxide. The chromium layer ranges in weight from about 0.1 to about 2.0 mg. of metallic chromium per square foot of article surface, and the hydrated chromium oxide layer contains from about 0.1 to 30 mg. of chromium values per square foot of article surface.

#### DESCRIPTION

The present invention provides an aqueous electrochemical bath and process by the use of which, in a sim-

ple, convenient, controllable, low cost operation, there is provided a surface-treated flat-rolled steel product, suitable for can manufacture, and having deposited thereon both a metallic chromium layer and an overlying chromium-containing oxide film.

The bath contains chromium trioxide (chromic acid),  $\text{CrO}_3$ , as the readily available, low cost chromium-containing constituent, and in a relatively low concentration, i.e., most broadly from about 5 to about 80 g./l., and preferably from about 15 to about 25 g./l.

The electrochemical coating bath of the invention also comprises, as the only other essential constituent, as a combined metallic chromium deposition catalyst and a promoter of the rapid formation of a uniform chromium-containing oxide film, a material selected from the group consisting of cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and sulfamic acid,  $\text{H}_2\text{NSO}_3\text{H}$ . No pretreatment of such baths are required.

It has been found that, when either cobaltous chloride or sulfamic acid, in an amount of from about 0.25 to about 5.0 g./l., preferably from about 0.25 to about 1.0 g./l. of cobaltous chloride or from about 0.25 to about 2.0 g./l. of sulfamic acid, is provided in the electrochemical treating bath of the invention, such materials, in the course of performance of the inventive process, as hereinafter described, cause a vigorous formation of a double-layered chromium—hydrated chromium oxide coating on the surface of the steel strip being treated. Among those knowledgeable in the art of metal surface treatment, it is well known that steel from different coils, such as coils of flat-rolled steel of can-stock gauges, e.g. 5 to 10 mils in thickness, even if ostensibly produced in the same manner, and by means of the same equipment, will frequently have quite different surface characteristics, so that a given surface treatment, applied to such coils, will produce markedly different results. Obviously, then, any surface treatment such as an electrolytic treatment, in order to provide an altered steel surface of the desired uniform properties, must be capable of fast and accurate response to such input variations. The action of the electrochemical baths of this invention is sufficiently fast in operation and consistent in result produced under a given set of operating conditions, e.g. current density, and those conditions are so readily and quickly changed in response to a change in surface reactivity of steel being treated, that the invention can be practiced under a wide range of conditions, to produce a usefully wide range of products, each of which is predictably consistent in properties. Indeed, the operating conditions of the inventive process are sufficiently flexible that the invention can be practiced with existing continuous steel strip electroplating facilities with only minor changes, if any.

In accordance with the process of the invention, steel strip, e.g. plain carbon steel black plate, is subjected to usual pre-plating cleaning steps, e.g. electrolytic alkaline treatment, rinse, cathodic acid treatment and rinse, and the strip is then introduced, as cathode, and in continuous fashion, between insoluble, e.g. lead, anodes into the inventive electrochemical bath. The acid pre-treatment may be omitted.

Total treating time in the latter bath is most broadly between about 0.25 and 10 seconds, although bath residence times of 3 seconds and under are preferred for economic reasons and are sufficient for the application of most coatings for can fabrication purposes.

The current density applied to the cathodic strip in the treating bath may range from about 25 to about 300 a.s.f. since, below 25 a.s.f. insufficient coating coverage is experienced, and best chromium plating efficiencies, bright metallic chromium surfaces, and optimum oxide production is not realized at current densities over about 300 a.s.f.

Residence time of the strip in the bath and magnitude of the applied current density are selected within the above-provided ranges of each such that the total coulomb-

bic input to the strip in the bath is from about 50 to about 1000 coulombs/ft.<sup>2</sup>.

The bath temperature is preferably maintained between about 70° and 190° F. in order to maintain best strip coating efficiency and to maintain a bright metallic appearance of the chromium layer.

As a part of the cleaning pretreatment, the steel to be electrochemically treated in the aforesaid bath may beneficially be given an anodic flash treatment prior to entry of the steel article into the coating bath. It has been found that adherence of the subsequently produced chromium oxide film is greatly improved by such treatment, thus inhibiting removal or disruption of such oxide film in the course of post-plating operations, or by rolls and the like. Such anodic pre-treatment is most conveniently accomplished by immersing the steel strip, as anode, in a first pass zone containing the same electrolyte as used for the following plating treatment. Such operation avoids contamination of the plating bath electrolyte and eliminates the necessity of providing a separate pre-treatment tank. However, such other tanks, and other electrolytes could be used if desired. The anodic current density applied does not affect the quantity of metallic chromium or hydrated chromium oxide deposited in the electrochemical coating bath zone, and the magnitude and duration of such anodic current density application need be only sufficient to effect the aforesaid oxide film adherence enhancement.

Various post-coating treating steps may also be used, if desired, to impart additional or enhanced product characteristics, such as further enhancement of rust resistance, e.g. when most dilute chromium trioxide solutions are used in the electrochemical coating bath.

When performed in accordance with the aforesaid conditions, the process of the invention is productive of treated steel strip which meets all of the above-described requirements for use in the fabrication and use of food and beverage cans and the like. The double-layered coating applied in the electrochemical coating bath consists of a layer of metallic chromium deposited on the black plate surface and a film or layer of hydrated chromium oxides overlying the metallic chromium layer. Since this double-layered coating is formed in a single electrochemical treating zone, it is postulated that both layers form simultaneously and continuously, part of the chromium values in the bath being reduced to metallic chromium and a portion being incompletely reduced and forming the overlying hydrated chromium oxides, although the invention is not limited to this proposed explanation.

The metallic chromium layer so produced ranges in weight from about 0.1 to about 2.0 mg. of chromium per square foot of article surface, and the overlying hydrated chromium oxide film ranges in weight from about 0.1 to about 30 mg. of chromium values (Cr+++ ) per square foot of article surface. Preferred coatings consist of those wherein the metallic chromium layer is from about 0.20 to about 1.5 mg. of chromium per square foot and the hydrated chromium oxide layer contains from about 2.0 to about 15.0 mg. of chromium values per square foot.

The most useful coatings are those wherein the hydrated chromium oxide film is so thin, generally under about 15 mg. of chromium per square foot, that the film produces an interference color on the surface of the treated article, imparting to the article a most pleasing and beautiful appearance. By varying the oxide film thickness, a wide range of colors can be produced. Color change is very sharp and sensitive to oxide film thickness, an oxide film thickness change of only about 2.0 mg. Cr+++ /ft.<sup>2</sup> causing a change in color from deep violet to light blue. Thus, the same appearance can be imparted to each coil of steel treated, regardless of its original surface reactivity, by merely adjusting the coulombic treating level imparted to each coil until the desired color intensity, corresponding to a certain chromium oxide film thickness, is obtained. The desired color can be produced

by detecting color changes in the treated strip either visually or by suitable optical instrumentation, and coulombic input to the strip in the electrochemical coating bath can then be varied manually or automatically, in accordance with the detected color changes. These colors, being interference colors, disappear after application of the final lacquer coating by the can manufacturer and do not then alter the metallic appearance of the metallic chromium layer as seen through a transparent lacquer coating.

The following specific examples are illustrative of the new electrochemical coating baths and the practice of the inventive process.

#### Example 1

Commercially produced, double cold-reduced plain carbon steel of 60 pound basis weight gauge (6.7 mils thickness), was given a preplating processing common to tinning quality black plate (except for acid pickling), i.e., it was electrolytically cleaned in alkaline solution and water rinsed. It was then given an anodic flash, at a current density of 170 a.s.f. for 0.67 second (114 coulombs/ft.<sup>2</sup>), in an electrochemical treating tank (containing the same electrolytic bath as given below). The cleaned strip was then treated in an aqueous electrochemical coating bath as follows:

Process element	Element specification
Chromium trioxide, CrO <sub>3</sub>	g./l. 60
Cobaltous chloride, CoCl <sub>2</sub> ·6H <sub>2</sub> O	g./l. 0.5
Cathodic current density	a.s.f. 100
Cathodic treating time	seconds 2.0
Solution temperature	° F. 120
Line speed	f.p.m. 150
Coulombs per square foot (cathodic pass)	340

#### Example 2

Steel strip similar to that of Example 1 was given the same pretreatment, except that the anodic flash was at a current density of 87 a.s.f. (58 coulombs/ft.<sup>2</sup>), and then cathodically treated in an aqueous bath as follows:

Process element	Element specification
Chromium trioxide	g./l. 20
Sulfamic acid	g./l. 1.0
Cathodic current density	a.s.f. 100
Cathodic treating time	seconds 2.0
Solution temperature	° F. 140
Line speed	f.p.m. 150
Coulombs per square foot (cathodic pass)	200

#### Example 3

Steel strip similar to that of Examples 1 and 2 was given the same pretreatment, except that the anodic flash was for 1.0 second at a current density of 85 a.s.f. (85 coulombs/ft.<sup>2</sup>), and then cathodically treated in an aqueous bath as follows:

Process element	Element specification
Chromium trioxide	g./l. 5.0
Cobaltous chloride	g./l. 0.25
Cathodic current density	a.s.f. 127
Cathodic treating time	seconds 3.0
Solution temperature	° F. 120
Line speed	f.p.m. 100
Coulombs per square foot (cathodic pass)	381

In this Example 3, following the electrochemical coating treatment, the coated strip was rinsed, "squeegeed," and then passed into an aqueous chemical treating bath containing 10 g./l. of chromium trioxide, the strip was then again "squeegeed" and hot air dried.

The products produced by the use of the aforesaid exemplary electrochemical coating baths and processes, including weights of metallic chromium and hydrated chromium oxide layers produced, together with performance of those products when tested for can fabrication property requirements in accordance with certain test

procedures (as hereinafter described), are given in Table I below.

temperature of 150° F., for 1 and 2 hours. The samples were then removed, rinsed in cold water, blotted dry and

TABLE I

Example Number	Chromium, mg./ft. <sup>2</sup>				Peel strength, lbs. per ¼ inch of seam width <sup>1</sup>	Enamel process adhesion 1-hour test <sup>2</sup>		Citric acid test, line width, mm.		Humid storage test, 30 day grade <sup>3</sup>		Stack rust test, 60 day grade <sup>3</sup>	
	Metallic Cr layer		Cr+++ in oxide layer			Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
	Top	Bottom	Top	Bottom									
1	0.8	0.4	6.3	5.4	26	0	0	0.1	0.1	0	0	0	0
2	0.5	0.5	8.3	6.8	31	0	0	0.1	0.1	0	0	3	3
3	0.5	0.4	5.4	4.3	39	0	0	0.1	0.1	1	2	1	2

<sup>1</sup> Average of top and bottom.

<sup>2</sup> 0=No enamel removed; 10=All enamel removed.

<sup>3</sup> 0=No rust; 10=Heavy rust.

It will be seen from Table I that both a metallic chromium layer and an overlying chromium oxide layer was produced in the case of each of the above three exemplary processes of the invention, the metallic layer comprising from 0.4 to 0.8 mg. Cr/ft.<sup>2</sup>, and the oxide layer comprising from 4.3 to 8.3 mg. Cr+++/ft.<sup>2</sup> of treated article surface.

The products of the aforesaid examples of the inventive process were tested to determine their conformity to the necessary product characteristics, as above-described, for food and beverage container use, the test procedures being as follows, with results as given in Table I above.

#### ADHESIVE PEEL STRENGTH TEST

This test is used to measure the effect of the steel stock surface on the strength of a cemented, lap-jointed side seam in tin-free steel cans.

In accordance with this test, flat panel samples (4 x 6 inches) of the treated steel stock were dip-coated with a lacquer to be used as the protective coating on the fabricated can and for which the adhesion to the can stock was to be determined.

Such lacquered panels were air dried for 10 minutes at room temperature and then oven-cured at 415° F. for 30 minutes.

The panels were then cut into ¾ inch wide strips. Three nylon 11 pellets were heat-tacked to one of the lacquered strips for each of the treated steels to be tested, near one end thereof and equally spaced across the width of the strip. Another strip was positioned over the first and the two were wrapped in aluminum foil, clamped between heated (500° F.) platens (shimmed apart to maintain a 3 mil adhesive layer between the bonded test strips), the pressure raised to 8000 p.s.i.g. and held at that value for 3 seconds. The specimens were then removed and allowed to cool at room temperature.

The strength of the resulting adhesive bond was determined by means of a standard tensile testing device provided with a special 180° peeling mandrel and operated at a speed of 2 inches per minute.

As shown by the Table I data, such tests of the products of Examples 1-3, using several proprietary can-making quality adhesives, showed the samples to have peel strengths of from 26 to 39 pounds per inch of sample width—well above the minimum 25 pounds per inch requirement for steels of such thicknesses.

#### ACCELERATED SALT WATER (ENAMEL PROCESS ADHESION) TEST

This test is used to measure the degree of adhesion of can coating lacquers and enamels to the steel stock. Panel specimens, 4 x 6 inches, were provided with a dip-coating of a gold phenolic lacquer (No. 1457 "Gold Lacquer," manufactured by Interchemical Corporation, of Clifton, N.J.), thinned to give a coating weight, after baking, of 1.8-2.2 mg./in.<sup>2</sup> of panel surface area.

The panels were air dried for 10 minutes and then oven-cured for 10 minutes at 410° F.

The panels were then placed in an aqueous solution consisting of sodium chloride, 30 g./l., and 30% hydrogen peroxide, 10 ml./l., and maintained therein, at a

15 immediately subjected to the "Scotch Tape Test," wherein pressure-sensitive adhesive tape is applied to the sample and then quickly and forcibly removed.

As will be seen from the Table I data, the samples thereof, when subjected to the one hour test, showed no loss of lacquer.

#### CITRIC ACID TEST

25 This test is used to measure the resistance of the treated steel stock to undercutting of an overlying can coating lacquer or enamel by corrosive can contents, and simulates undercutting conditions encountered at the site of scratches, breaks or holes in the lacquer on carbonated beverage cans.

30 Panels were prepared and baked in the same manner as for the accelerated salt water test. Specimens 2 inches x 4 inches were taken from the panels and the lacquer cut through with a knife, making lines of 0.1 mm. width and extending (1) in the steel rolling direction, (2) across the rolling direction, and (3) diagonally to the rolling direction. The specimens were then placed, with the cut line face up, in an enameled tray containing a 3% citric acid solution, and stored for 96 hours at 75 to 80° F. The specimens were then removed, blotted dry, and the total width of the cut lines was measured with a 7 magnifying glass having an 0.1 mm. scale on its field.

35 Increase in scratched line width to more than 0.2 mm. is considered as excessively severe undercutting.

From the Table I data, it will be seen that in no instance did the width of the specimen lines increase measurably.

#### 45 HUMID STORAGE RUST RESISTANCE TEST

50 This test is used to determine the resistance of steel can stock to rusting during storage in a humid atmosphere and is thus a measure of the usefulness of a surface treatment to inhibit rusting during shipment and storage prior to lacquer application.

Unlacquered panels of the treated steels, in the form of 4 x 6 inch panels, were placed, at an angle of 15°, in slotted plastic racks with ½ inch separations between panels. The racks were placed in a sealed humidity cabinet at 100° F. and 85% relative humidity for 30 days.

55 Inspection of the data of Table I shows that no rusting was observed in the case of either the products of Example 1 or 2, and that there was only very slight rusting of the product of the Example 3 process (most dilute electrochemical bath, i.e. 5 g./l. CrO<sub>3</sub>).

#### 60 STACK RUST RESISTANCE TEST

65 This is a more severe rusting test and represents conditions that would rarely, if ever, be encountered under actual service conditions.

In accordance with this test, 4 inch x 7 inch panel samples of the treated steels, comprising five specimens of each material, were placed in a tight stack, and the stack placed in a sealed desiccator held at ambient room temperature and 100% relative humidity for 60 days.

70 As shown in Table I, no rusting, even under these severe conditions, was observed in the case of the product of Example 1, and only slight rusting was produced on the Example 2 and 3 products.

These processes of Examples 1-3 were conducted, and the products thereof produced, on a continuous pilot line basis. Additional, commercial-scale tests were also conducted, using an aqueous electrochemical treatment bath containing, as catalyst and film promoter, 1 g./l. of sulfamic acid, together with 20 g./l. of chromium trioxide, the bath being maintained at a temperature of 120° F. Other test parameters, together with a characterization of the products produced, are given below in Table II.

TABLE II

Example Number	Mill coil Number	Line speed, f.p.m.	Current density, a.s.f.		Treating time, secs.		Coulombs per ft. <sup>2</sup>		Chromium, mg./ft. <sup>2</sup> , coil average			
			Anodic pass	Cathodic pass	Anodic pass	Cathodic pass	Anodic pass	Cathodic pass	Metallic chromium		Cr++ in oxide	
									Top	Bottom	Top	Bottom
55#-1	737119	610	125	134	0.49	2.46	62	332	0.6	0.5	9.9	10.2
55#-2	737063	610	195	145	0.49	2.46	96	359	0.4	0.4	9.9	9.4
55#-3	737064	610	118	84	0.49	2.46	58	208	0.4	0.4	5.7	4.8
55#-4	737125	610	129	124	0.49	2.46	64	304	0.5	0.4	7.8	7.4

It will be seen from Table II, that, in the case of each example, a metallic chromium layer was deposited on the rapidly moving steel strip, such layer ranging in weight from 0.4 to 0.6 mg./ft.<sup>2</sup> of article surface. A hydrated chromium oxide layer was also produced in each instance, and varied in weight from 4.8 to 10.2 mg. Cr++/ft.<sup>2</sup> of article surface.

The results of property tests, in all respects as above-described, performed upon the further examples of Table II are given in Table III.

TABLE III

Example number	Peel strength lbs. per 3/4" (coil average) Top and Bottom	Enamel process adhesion test, 1 hour test <sup>1</sup> (coil average)		Citric acid test, line width, nm. (coil average)		Humid storage test, 30 day grade <sup>2</sup> (coil average)		Stack rust test, 60 day grade <sup>2</sup> (coil average)	
		Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
55#-1	22	0	0	0.1	0.1	3	2	2	2
55#-2	25	0	0	0.1	0.1	1	1	1	1
55#-3	36	0	0	0.1	0.1	1	2	2	2
55#-4	27	0	0	0.1	0.1	1	1	4	4

<sup>1</sup> 0=No enamel removed; 10=All enamel removed.

<sup>2</sup> 0=No rust; 10= Heavy rust.

As in the case of Table I examples, those of Tables II exhibited, as shown by the Table III data, good results in each test, indicating suitability of such products for food and beverage container manufacture.

It is to be understood that the foregoing examples and specific embodiments are merely illustrative of the principles of the invention, and that modifications thereof may be made by those skilled in the art without departing from the spirit and scope of the invention.

I claim:

1. A method for the production of corrosion-resistant, tin-free carbon steel stock suitable for the manufacture of food and beverage containers, comprising:

(a) continuously moving an elongated, cleaned flat-rolled steel black plate article, as cathode, through a cathodic electrochemical treating zone;

(b) immersing the article in the cathodic zone in an electrochemical treating bath contained therein and comprising an aqueous solution consisting essentially of from about 5 to about 80 g./l. of chromium trioxide and from about 0.25 to about 5 g./l. of a protective film-forming promoter selected from the group consisting of cobaltous chloride and sulfamic acid;

(c) applying to the cathodic article in the electrochemical treating bath an electrical current of a density of from about 25 to about 300 a.s.f.; and

(d) retaining the article in the bath under the influence of the electrical current for a time sufficient to provide an electrical energy input to the article of from about 50 to about 1000 coulombs/ft.<sup>2</sup> of article surface, whereby there is provided on the

steel article a double-layered protective coating comprising a layer of metallic chromium adjacent to the steel surface and a layer of hydrated chromium oxide overlying the metallic chromium layer.

2. A method in accordance with claim 1, wherein the black plate article is subjected to an electrochemical anodic treatment in a first treating zone prior to treatment in the cathodic zone.

3. A method in accordance with claim 2, wherein the

anodic treatment is carried out by immersing the article in a bath of the same composition as that contained in the cathodic treatment zone.

4. A method in accordance with claim 1, wherein the promoter is selected from the group consisting of from about 0.25 to about 1.0 g./l. of cobaltous chloride and from about 0.25 to about 2 g./l. of sulfamic acid.

5. A method in accordance with claim 4, wherein the temperature of the electrochemical treating bath is maintained between about 70 and 190° F.

6. A method in accordance with claim 1, wherein the hydrated chromium oxide layer exhibits an interference color, and comprising the further steps of:

(a) determining variations in color of the hydrated chromium oxide layer from a predetermined desired color; and

(b) adjusting the coulombic input to the article in the cathodic electrochemical treating zone in response to said determined color variations, and thereby controlling the thickness of the hydrated chromium oxide layer in accordance with a predetermined, desired thickness.

7. A method for the continuous production of corrosion-resistant, flat-rolled steel stock, comprising continuously passing a flat-rolled steel-base stock through an electrochemical treating bath comprising an aqueous solution consisting essentially of from about 5 to about 80 g./l. of chromium trioxide and from about 0.25 to about 5 g./l. of a promoter material selected from the group consisting of cobaltous chloride and sulfamic acid, while impressing upon the stock as cathode, an electrical current of about 25 to about 300 a.s.f. for a time of about 0.25 to about 10 seconds in order to apply a total of about 50 to about 1000 coulombs/ft.<sup>2</sup> of energy.

8. An electrochemical treatment bath comprising an aqueous solution consisting essentially of from about 5 to about 80 g./l. of chromium trioxide and from about 0.25 to about 5.0 g./l. of cobaltous chloride.

9. A bath in accordance with claim 8, wherein the cobaltous chloride is present in an amount of from about 0.25 to about 1.0 g./l.

(References on following page)

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References Cited

UNITED STATES PATENTS

2,682,503	6/1954	Hesch	-----	204—58	XR
2,784,153	3/1957	DuRose	-----	204—51	
3,081,238	3/1963	Gurry	-----	204—34	
3,113,845	12/1963	Uchida et al.	-----	204—34	XR
3,296,100	1/1967	Yonezaki et al.	-----	204—41	
3,316,160	4/1967	Uchida et al.	-----	204—28	
3,450,610	6/1969	Fröden	-----	204—34	XR

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OTHER REFERENCES

Edwin J. Smith, Iron and Steel Engineer, pp. 125-130, July 1967.

GERALD L. KAPLAN, Primary Examiner

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204—34, 41, 51, 56