

1

2,906,677

ELECTROLYTIC TREATMENT OF TINPLATE

Edwin J. Smith, Steubenville, Ohio, and John R. Smith, Weirton, W. Va., assignors to National Steel Corporation, a corporation of Delaware

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The present invention relates to an improved method of electrolytically treating tinplate for improving the qualities of the tinplate, to a novel electrolyte bath for electrolytically treating tinplate, and to the treated tinplate product.

Although the invention is primarily concerned with treating strip tinplate produced by a continuous electroplating process, it is not limited to such tinplate and its principles are applicable to electrolytic tinplate produced by other electroplating processes, tinplate produced by the hot-dip process, and to other articles presenting a tin surface or an alloy surface that is predominately tin.

Large quantities of tinplate are produced by both the hot-dip process and the electrolytic process. A large percentage of the tinplate used for cans and other containers, in particular those containers for food and beverages, is produced commercially by the electroplating of strip. In producing electrolytic tinplate commercially, a continuous strip of base metal, such as blackplate, is progressively moved through a long electroplating line. As the strip moves through the line, usually at speeds of one thousand feet per minute and upward, it is cleaned, pickled, scrubbed, and then electroplated with a coating of tin. After the strip has been plated, usually on both surfaces, it is washed to remove any residual electrolyte and the tin coating is flow brightened to convert the tin from a condition in which it presents a matte surface to a condition in which it presents a bright mirror-like surface. The flow brightening is effected by melting and then solidifying the tin coating. The flow brightened tinplate strip is coiled into large coils and is subsequently trimmed, cut and thereafter processed to form the containers or the strip may be trimmed and cut without coiling.

As in the case of other metals, the initial bright mirror-like surface of tinplate will revert to the oxide of the metal and as the oxidation process progresses, various colors develop on the thin surface. The first visible color is yellow. As the oxidation process progresses, the color changes from yellow through brown and purple to blue. Inasmuch as the yellow color is most common, such oxide films are generally known as "yellow discoloration" or "yellow stain." A further distinction is sometimes made, in that discoloration arising from lacquer baking operations is called "baking discoloration" and discoloration developed during storage is called "warehouse discoloration." The term "yellow discoloration" as used herein including the claims is intended to cover discoloration resulting from surface oxidation of tinplate and includes oxidation occurring during storage as well as oxidation arising during baking.

2

A number of chemical and electrochemical filming methods have been developed in the prior art for the purpose of retarding the growth of undesirable oxide films on tinplate surfaces and thereby minimizing yellow discoloration. The most successful of these methods requires the presence of a chromate in the chemical treating agent or electrolyte, there being an invisible but measurable amount of chromium deposited on the tinplate surface. Although these chromium containing films are satisfactory for minimizing yellow discoloration, they are thought by many to leave much to be desired. For example, the presence of the chromate is thought by some to bring about an undesirable catalytic effect on the drying properties of organic finishes including lacquers. Despite such objections, chromate containing films continue to serve their purpose since no satisfactory substitute has been found.

Besides the requirement that the yellow discoloration quality of tinplate be improved, certain uses of tinplate require that its resistance to sulfide staining and to acid attack be improved. At the same time it is often desirable that bleaching of highly colored fruits or other food packed in tin containers be eliminated. Although it would be possible to produce tinplate having high resistance to sulfide staining, it is generally considered more satisfactory to lacquer the tinplate to minimize sulfide staining and at the same time eliminate bleaching of the food pack. In order to do this, it is essential that the treated tinplate have satisfactory lacquer adhesion as well as adequate resistance to yellow discoloration. For this reason, any treatment of tinplate intended to afford protection against yellow discoloration should still give satisfactory lacquer adhesion properties when desired.

Accordingly, it is an object of the present invention to provide an improved method for electrolytically treating tinplate in a chromate-free bath for the purpose of improving its resistance to yellow discoloration.

Another object of the present invention is to provide an improved process of forming a chromate-free film on the surface of tinplate for the purpose of improving its resistance to yellow discoloration and characterized by the ability when operated under controlled conditions to produce satisfactory lacquer adhesion properties.

Another object of the present invention is to provide an improved process as aforesaid further characterized by its ability to treat tinplate strip moving at a high speed through an electroplating line.

Another object of the present invention is to provide a chromate-free bath in which tinplate can be electrolytically treated to produce an improved product characterized by improved resistance to yellow discoloration.

Another object of the present invention is to provide a chromate-free bath in which tinplate can be electrolytically treated to produce an improved product characterized by resistance to yellow discoloration and satisfactory lacquer adhesion properties.

Another object of the present invention is to provide an improved bath as aforesaid further characterized by its ability to treat tinplate strip moving at a high speed through an electroplating line.

Another object of the present invention is to provide a tinplate product characterized by improved resistance to yellow discoloration and obtained by electrolytic treatment of tinplate in a chromate-free electrolyte bath.

Another object of the present invention is to provide a tinplate product characterized by improved resistance to yellow discoloration and satisfactory lacquer adhesion properties and obtained by electrolytic treatment of tinplate in a chromate-free electrolyte bath.

These and other objects will become more apparent upon considering the following description of the invention.

In accordance with the present invention, proper electrolytic treatment of tinplate in an aqueous, chromate-free bath containing both sodium dihydrogen phosphate and sodium nitrate improves its resistance to yellow discoloration. Treatment under certain preferred conditions obtains satisfactory lacquer adhesion as well as improved resistance to yellow discoloration.

While the present invention will be discussed in connection with the use of sodium dihydrogen phosphate and sodium nitrate, it will be understood that the corresponding potassium salts, potassium dihydrogen phosphate and potassium nitrate, may be used to replace all or part of their corresponding sodium salts. Where a potassium compound is substituted for its sodium compound, the quantity of the potassium salt used should be adjusted so as to provide an equivalent amount of phosphate or nitrate as the case may be. When referring to quantities and unless otherwise stated, the phosphate salt is calculated as NaH_2PO_4 and the nitrate is calculated as NaNO_3 . Water of crystallization is not included in the calculations.

It is essential that the aqueous bath in which the tinplate is treated include both sodium dihydrogen phosphate and sodium nitrate. These salts may be added as such or formed in situ. Good results have been obtained when using from 1 to 6 ounces of sodium dihydrogen phosphate per gallon of solution. Higher concentrations of sodium dihydrogen phosphate may be employed but are not economical. Lower concentrations do not obtain sufficient residual phosphate on the tinplate to offer commercially adequate protection against yellow discoloration.

The amount of sodium nitrate present in the bath of the present invention may vary from 1 part by weight of nitrate to each 30 parts by weight of sodium dihydrogen phosphate up to equal parts by weight of nitrate and phosphate. As will be discussed more fully hereinafter, the anodic and cathodic treatment values employed for treating tinplate in the electrolyte of the present invention may vary from 1 to 12 ampere seconds per square foot of surface treated. In the case of using an anodic treatment value greater than 6 ampere seconds per square foot, the highest concentration of nitrate possible while avoiding pitting of the tinplate is 1 part by weight of sodium nitrate for each 3 parts by weight of sodium dihydrogen phosphate. The sodium nitrate constituent of the bath of the present invention functions as an accelerator in that it permits a wider variation of current conditions to be employed.

In accordance with the method of the present invention, tinplate is treated in the above-described aqueous acidic bath by functioning first as an anode and then as a cathode while controlling the anodic and cathodic treatments so as to meet certain critical limitations. In the event that the tinplate alternately functions as an anode and cathode, the last function must be as a cathode.

When the tinplate is made an anode and proper anodic treatment is employed, a phosphate containing coating or film is formed on the surface of the tinplate. At the same time, tin oxide is also formed. If the resultant tinplate is then made a cathode in the same or another electrolyte bath of the present invention and proper cathodic treatment is employed, the oxide content of the film may be reduced to a fairly low level without adversely affecting the phosphate film. The resulting tinplate has good resistance to yellow discoloration. The tinplate also has sulphide stain and abrasion resistances comparable to those obtainable in the commercially accepted acid

chromate treated tinplates. If good lacquer adhesion is also desired, this may be obtained by proper selection of the concentration of the constituents in the electrolyte bath and control of the anodic and cathodic treatment values employed as more fully explained hereinafter.

For the purpose of treating the tinplate as an anode in the electrolyte bath, anodic treatment values ranging from 1 to 12 ampere seconds per square foot of surface area treated are necessary. The use of anodic treatment values of less than one ampere second per square foot obtains films of poor resistance to yellow discoloration. Higher anodic treatment values on the other hand deposit phosphate films whose oxide values are such as to interfere with the subsequent necessary cathodic treatment of the tinplate. When employing an anodic treatment value of 6 ampere seconds per square foot and greater, it is essential that the ratio of nitrate to phosphate be not greater than 1:3. This is to eliminate pitting of the tinplate surface.

After the anodic treatment of the tinplate, it is treated as a cathode in the same or another electrolyte having a composition falling within the above described limits. The cathodic treatment values for this cathodic treatment also range from 1 to 12 ampere seconds per square foot of area treated. A minimum of 1 ampere second per square foot is required to reduce the oxide formed by the anodic treatment to a value which is acceptable. On the other hand, use of a cathodic treatment value greater than 12 ampere seconds per square foot alters the phosphate film to an extent that it is no longer effective in preventing yellow discoloration.

From the foregoing, it would be expected that the higher the anodic treatment value used in the anodic treatment, the heavier the phosphate film obtained. Actually, optimum anodic treatment conditions for heavy phosphate filming require the use of anodic treatment values of intermediate value ranging from 5 to 7 ampere seconds per square foot, 6 ampere seconds per square foot being the optimum anodic treatment value for a bath containing from 1 to 6 ounces of sodium dihydrogen phosphate per gallon of solution and up to 1 part by weight of sodium nitrate for each 3 parts by weight of sodium dihydrogen phosphate. Although the cathodic treatment when maintained within the range of from 1 to 12 ampere seconds per square foot has no substantial effect on the weight of phosphate film retained on the tinplate, it is found that the lower the cathodic treatment value, the higher the phosphate coating weight on the tinplate. Thus a cathodic treatment value range of from 1 to 3 ampere seconds per square foot is preferred.

Operation within the aforesaid bath concentration and anodic and cathodic treatment value ranges obtains a film on tinplate which is highly resistant to yellow discoloration. However, when lacquer adhesion is also of importance to the finished product, it is necessary to operate at certain anodic and cathodic treatment values within the above ranges. The optimum anodic and cathodic treatment value ranges for obtaining satisfactory lacquer adhesion properties include from 1 to 3 ampere seconds per square foot anodic treatment followed by a cathodic treatment of from 1 to 12 ampere seconds per square foot. The preferred cathodic treatment value range for obtaining highly satisfactory lacquer adhesion properties is from 1 to 3 ampere seconds per square foot.

In the tables presented hereinafter, certain terms are used for the purpose of explaining the procedure employed and for evaluating the tests performed on the tinplate samples. The following definitions explain the meaning of these terms.

Yellow discoloration test.—In this test, the samples are placed in an electrically heated oven and maintained at a temperature of 410° F. for 30 minutes. At the end of this time, the samples are withdrawn and allowed to air cool. If the samples so tested present a bright, mirror-like surface and show no traces of yellow stain formation,

then they are sufficiently resistant to yellow discoloration to meet commercial requirements. Alternatively, the nonlacquered surface of the samples used to determine lacquer adhesion may be examined to determine resistance to yellow discoloration.

Lacquer adhesion test.—In this test, a layer of a phenol-aldehyde type lacquer is applied with a roller to each of the samples. The amount of lacquer applied is such that after baking, there is a film present on each sample weighing about one and one half milligrams per square inch. After the lacquer has been applied to the samples they are dried at atmospheric temperature to a substantially non-tacky condition and are then baked at 410° F. for 10 minutes. The lacquer coating on each sample is then cut or scratched and a strip of tape is applied to the coating and the tape extended across the scratch. This tape is of the type customarily known as "Scotch tape" and consists of a layer of backing material coated with a pressure sensitive adhesive. The tape used was three quarters of an inch wide and required a pull of about 40 pounds to strip it from a sample. After the tape has been applied to the scratched coating, it is quickly torn off. This test is a comparative test and indicates the comparative degree of lacquer adhesion. Under the conditions set forth, if no film of lacquer adheres to the tape when it is torn off, the lacquer adhesion is considered to be perfect and is evaluated by the numeral 0. If not more than 2 percent of the film covered by the tape is removed by the tape, the lacquer adherence is considered satisfactory and is evaluated by the numeral 1. A numeral evalua-

ned to the source of current as a cathode. The current density in amperes per square foot is varied according to variations in the line speed so as to obtain operating conditions of from 1 to 12 ampere seconds per square foot. This value is obtained by multiplying the treating time in seconds by the current density in amperes per square foot. Subsequent to the above described single anodic treatment and in the same bath if desired, the strip is connected to a source of direct current as a cathode and moves between additional spaced insoluble bars connected to the source of current as anodes. The current density in amperes per square foot is also varied according to the variations in the line speed so that the ampere seconds per square foot are maintained within the range of from 1 to 12. Subsequent to this single cathodic treatment the strip is rinsed and dried.

In the tables presented hereinafter, samples of the above described untreated tinplate were cut into 8 inch squares, duplicate samples being made for each treatment. These samples were treated in baths of varying concentrations as set forth hereinafter and at the indicated anodic and cathodic treatment values. The treated samples were washed and dried and were then evaluated for phosphate film content, oxide content of the film, yellow discoloration resistance, lacquer adhesion, abrasion resistance, and sulphide staining resistance.

A summary of the phosphate analysis of samples treated in accordance with the present invention with the phosphate expressed in terms of micrograms per square foot is as follows:

Table I

Current, amp. sec./sq. ft.	3 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃	1 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃	6 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃	3 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃	3 oz./gal. NaH ₂ PO ₄ + 3 oz./gal. NaNO ₃
1.2 anodic.....	174	139	199	130	132
1.2 cathodic.....					
1.2 anodic.....	163	137	222	121	164
6 cathodic.....					
1.2 anodic.....	163	146	249	139	155
12 cathodic.....					
6 anodic.....	298	326	312	372	158
1.2 cathodic.....					
6 anodic.....	265	245	222	295	240
6 cathodic.....					
6 anodic.....	215	234	217	231	240
12 cathodic.....					
12 anodic.....	223	238	302	314	
1.2 cathodic.....					
12 anodic.....	176	169	388	216	
6 cathodic.....					
12 anodic.....	130	197	217	163	
12 cathodic.....					

tion of 10 represents a complete lacquer failure. Values of 0 and 1 are considered to be commercially acceptable.

Sulphide staining test.—The resistance to sulphide staining may be tested in a number of ways. For example, the samples may be inserted in cans packed with peas and then processed at 240° F. for 60 minutes. If the tinplate meets this test without undue staining, it is considered sufficiently resistant to sulphide staining for most commercial applications.

Treatment conditions.—The tinplate used in obtaining data for the following tables was 0.75 pound per base box tinplate which was nonchemically treated and was obtained from a regular production supply run. This tinplate had been produced in a strip electroplating line as described previously.

In the case of a continuous operation, the strip is passed through a chromate-free bath containing an aqueous solution of sodium dihydrogen phosphate and sodium nitrate in specified proportions. As it is passed through this bath, it is connected to a source of direct current as the anode and moved between spaced insoluble bars con-

All of the above samples had good resistance to yellow discoloration. The heaviest phosphate film weights were obtained when employing intermediate anodic treatment values ranging from 5 to 7 ampere seconds per square foot. The ampere seconds per square foot of cathodic treatment employed does not have as great an effect on the phosphate coating weight as does the value of the anodic treatment employed. However, cathodic treatment values of from 1 to 3 ampere seconds per square foot are preferred. When employing anodic treatment values of 6 ampere seconds per square foot and greater, if more than 1 part by weight of sodium nitrate is present for each 3 parts by weight of sodium dihydrogen phosphate, pitting occurs.

The following tabulated data illustrates the tin oxide content of the chemical film on the treated tinplate when employing anodic and cathodic treatments and bath concentrations identical with those of Table I. The unit of measurement of the oxide film is expressed in milli-coulomb equivalents per square inch (MCE/sq. inch) for both tinplate surfaces.

Table II

Current, amp. sec./sq. ft.	3 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃	1 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃	6 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃	3 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃	3 oz./gal. NaH ₂ PO ₄ + 3 oz./gal. NaNO ₃
1.2 anodic.....	5.6/6.25	5.6/5.0	6.9/6.9	6.25/8.1	6.25/6.25
1.2 cathodic.....					
1.2 anodic.....	5.6/5.6	5.6/5.0	7.5/6.9	5.6/5.0	7.5/7.5
6 cathodic.....					
1.2 anodic.....	5.6/5.6	6.9/6.25	6.9/6.9	5.6/5.0	7.5/7.5
12 cathodic.....					
6 anodic.....	3.8/3.8	4.4/5.0	6.25/7.5	6.25/5.6	8.1/6.9
1.2 cathodic.....					
6 anodic.....	5.6/5.6	5.6/6.25	6.25/6.9	5.0/5.0	6.9/6.25
6 cathodic.....					
6 anodic.....	5.0/5.6	6.25/7.5	6.25/7.5	6.25/6.25	6.25/7.5
12 cathodic.....					
12 anodic.....	4.4/5.0	5.6/5.6	7.5/7.5	6.25/6.25	-----
1.2 cathodic.....					
12 anodic.....	5.0/6.25	6.25/5.6	6.9/7.5	7.5/6.9	-----
6 cathodic.....					
12 anodic.....	5.0/5.0	6.25/6.9	8.1/7.5	5.6/5.6	-----
12 cathodic.....					

From the foregoing it is apparent that the oxide contents of the protective films of the present invention are of relatively low and uniform value on both sides of the sample.

The following tabulated data employing anodic and cathodic treatments and bath concentrations identical with Tables I and II is for the purpose of illustrating the phenol-aldehyde lacquer adhesion properties of the samples treated. The two indicated values for each anodic and cathodic treatment and bath concentration are for separate tests on the same surface of the sample.

hesion suffices to meet the requirements of commercial tinplate since the lacquer coating minimizes the sulphide stain problem as well as the problem of food pack bleach.

The foregoing description of the present invention and the tables are for the purpose of illustration and are not limiting to the scope of the present invention which is set forth in the claims.

We claim:

1. The method of improving the yellow discoloration resistance of tinplate which comprises the steps of anodi-

Table III

Current, amp. sec./sq. ft.	3 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃		1 oz./gal. NaH ₂ PO ₄ + 0.1 oz./gal. NaNO ₃		6 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃		3 oz./gal. NaH ₂ PO ₄ + 1 oz./gal. NaNO ₃		3 oz./gal. NaH ₂ PO ₄ + 3 oz./gal. NaNO ₃	
1.2 anodic.....	1	1	0	0	1	1	0	0	0	0
1.2 cathodic.....										
1.2 anodic.....	1	3	0	1	2	2	0	1	0	0
6 cathodic.....										
1.2 anodic.....	2	2	0	0	1	0	1	1	0	0
12 cathodic.....										
6 anodic.....	5	5	10	10	10	10	10	9	1	1
1.2 cathodic.....										
6 anodic.....	3	1	10	10	5	6	10	10	2	2
6 cathodic.....										
6 anodic.....	7	8	5	5	1	2	2	2	3	3
12 cathodic.....										
12 anodic.....	10	10	10	10	10	10	10	10	-----	-----
1.2 cathodic.....										
12 anodic.....	4	4	5	9	5	5	2	1	-----	-----
6 cathodic.....										
12 anodic.....	2	1	3	3	5	4	2	1	-----	-----
12 cathodic.....										

From the data of Table III it is apparent that over the range of operative bath compositions, both anodic and cathodic treatment values should be maintained at a fairly low level in order to obtain maximum lacquer adhesion properties. Thus for example, an anodic treatment of from 1 to 3 ampere seconds per square foot followed by a cathodic treatment of from 1 to 3 ampere seconds per square foot obtains optimum lacquer adhesion along with acceptable yellow discoloration resistance.

The foregoing tables illustrate the yellow discoloration resistance and lacquer adhesion properties of tinplate treated in accordance with the present invention. The sulphide stain and abrasion resistances of these samples are completely comparable with sulphide stain and abrasion resistances of tinplate treated with the accepted acid-chromate containing treating agent. As explained hereinbefore, the sulphide stain resistance of the commercially treated tinplate of today leaves much to be desired. However, the sulphide stain resistance of the tinplate treated in accordance with the present invention is comparable and as explained, good resistance to yellow discoloration with good lacquer ad-

cally treating tinplate in an aqueous chromate-free, acidic bath and finally cathodically treating the anodically treated tinplate in an aqueous chromate-free, acidic bath, the anodic and cathodic treatment values ranging from 1 to 12 ampere seconds per square foot of surface area treated, the aqueous chromate-free acidic bath in each of the treatments consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate dissolved in the aqueous bath as additive ingredients, the amount of dihydrogen phosphate in the bath ranging from 1 to 6 ounces per gallon of solution when calculated as sodium dihydrogen phosphate, the ratio by weight of phosphate to nitrate ranging from 30:1 to 1:1 when calculated on the basis of the sodium salts for all anodic treatment values up to 6 ampere seconds per square foot, and the ratio by weight of phosphate to nitrate ranging from 30:1 to 3:1 when calculated on the basis of the sodium salts for anodic treatment values of at least 6 ampere seconds per square foot.

5. The method of improving the yellow discoloration

8. The method of improving the yellow discoloration resistance of tinplate which comprises the steps of anodically treating tinplate in an aqueous chromate-free, acidic bath and finally cathodically treating the anodically treated tinplate in an aqueous chromate-free, acidic bath, the anodic treatment value ranging from 5 to 7 ampere seconds per square foot of surface area treated, the cathodic treatment value ranging from 1 to 3 ampere seconds per square foot of surface area treated, the aqueous chromate-free acidic bath in each of the treatments consisting essentially of sodium dihydrogen phosphate and sodium nitrate dissolved in the aqueous bath as additive ingredients, the amount of sodium dihydrogen phosphate in the bath ranging from 1 to 6 ounces per gallon of solution, the ratio by weight of sodium phosphate to sodium

11

nitrate ranging from 30:1 to 1:1 for all anodic treatment values up to 6 ampere seconds per square foot, and the ratio by weight of sodium phosphate to sodium nitrate ranging from 30:1 to 3:1 for anodic treatment values of at least 6 ampere seconds per square foot.

9. The method of improving the yellow discoloration resistance of tinplate while obtaining satisfactory lacquer adhesion properties which comprises the steps of anodically treating tinplate in an aqueous chromate-free, acidic bath and finally cathodically treating the anodically treated tinplate in an aqueous chromate-free, acidic bath, the anodic treatment value ranging from 1 to 3 ampere seconds per square foot of surface area treated, the cathodic treatment value ranging from 1 to 12 ampere seconds per square foot of surface area treated, the aqueous chromate-free acidic bath in each of the treatments consisting essentially of sodium dihydrogen phosphate and sodium nitrate dissolved in the aqueous bath as additive ingredients, the amount of sodium dihydrogen phosphate in the bath ranging from 1 to 6 ounces per gallon of solution, the ratio by weight of sodium phosphate to sodium nitrate ranging from 30:1 to 1:1 for all anodic treatment values.

10. The method of improving the yellow discoloration resistance of tinplate while obtaining satisfactory lacquer adhesion properties which comprises the steps of anodically treating tinplate in an aqueous chromate-free, acidic bath and finally cathodically treating the anodically treated tinplate in an aqueous chromate-free, acidic bath, the anodic treatment value ranging from 1 to 3 ampere seconds per square foot of surface area treated, the cathodic

12

treatment value ranging from 1 to 3 ampere seconds per square foot of surface area treated, the aqueous chromate-free acidic bath in each of the treatments consisting essentially of sodium dihydrogen phosphate and sodium nitrate dissolved in the aqueous bath as additive ingredients, the amount of sodium dihydrogen phosphate in the bath ranging from 1 to 6 ounces per gallon of solution, the ratio by weight of sodium phosphate to sodium nitrate ranging from 30:1 to 1:1 for all anodic treatment values.

11. The tinplate product of improved yellow discoloration resistance as produced by the method of claim 1.

12. The tinplate product of improved yellow discoloration resistance as produced by the method of claim 2.

13. The tinplate product of improved yellow discoloration resistance as produced by the method of claim 3.

14. The tinplate product of improved yellow discoloration resistance as produced by the method of claim 4.

15. The tinplate product of improved yellow discoloration resistance as produced by the method of claim 5.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,906,677

September 29, 1959

Edwin J. Smith et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 52, for "thin" read -- tin --.

Signed and sealed this 27th day of June 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

