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[54] **METHOD FOR ELECTROCHEMICAL PASSIVATION OF TINPLATE AND ELECTROLYTE FOR USE THEREIN**

[75] Inventors: **Franz Jargon,** Schwanewede; **Erich Maschke,** Bremen; **Rudolf Eylens,** Leuchtenberg, all of Germany

[73] Assignee: **Klockner-Werke AG,** Duisburg, Germany

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[56] **References Cited**

UNITED STATES PATENTS

2,437,620	3/1948	Speer	204/58
2,746,915	5/1956	Giesker et al.	204/56 R
3,278,401	10/1966	Smith et al.	204/56 R

Primary Examiner—R. L. Andrews
Attorney, Agent, or Firm—Michael S. Striker

[57] **ABSTRACT**

A method for treating a material having a tin-containing surface to passivate and improve the corrosion resistance of the said surface which comprises making the material a cathode in an aqueous hexavalent chromium electrolyte consisting essentially of an aqueous solution of an alkali-metal dichromate in an amount of at least 20 and at most 25 grams per liter, an alkali-metal acetate in an amount of at least 5 and at most 10 grams per liter, and chromium trioxide in an amount of approximately 5 grams per liter, the said electrolyte having a hydrogen-ion concentration corresponding to a pH between 4.0 and 5.0 and an electrical conductivity of at least 28,000, preferably above 30,000, micromhos per centimeter at a temperature of 50° C, and passing an electric current through the material and the electrolyte until an amount of a chromium-containing film is deposited upon the said surface that is sufficient to improve the corrosion resistance of the said material.

8 Claims, No Drawings

METHOD FOR ELECTROCHEMICAL PASSIVATION OF TINPLATE AND ELECTROLYTE FOR USE THEREIN

INTRODUCTION

The present invention pertains to the electrochemical passivation of tinplate and similar materials having a tin-containing surface to improve their resistance to corrosion so that they may be improved with respect to their suitability for use for the production of containers for use in the canning and packaging of foodstuffs, particularly protein-containing foodstuffs.

BACKGROUND OF THE INVENTION

Tinplate is made by coating iron or steel sheet materials with a film of tin, either by dipping the sheet into molten tin or by an electroplating operation. The amount of tin that is usually deposited in between 0.125 and 1.0 pound per base box (62,720 square inches) which is equivalent to between 1.40 and 11.21 grams per square meter of the material. The thus-coated sheet material has a bright glossy surface.

In the absence of atmospheric oxygen or oxidizing agents, tin, unlike iron, acts as an anode in the presence of organic acids such as are present in foodstuffs. Because of its higher hydrogen overvoltage (1.22 volts compared to 0.82 volt for iron at 25°C in 2-normal sulfuric acid at 10 amperes per square decimeter) the polarization of tin is changed. Because of this, tinplate is suitable for use as a packaging material for foodstuffs. It can be cold-worked, bent, and folded and sealed or welded together and meat and other foodstuffs do not readily adhere thereto.

Tinplate, however, has a tendency to stain by formation of tin sulfide when fish, meat, milk and certain vegetables containing proteins which include a sulfur-containing amino acid component are placed into contact therewith. Such staining is also referred to as marbling.

Conventional electrochemical aftertreatment of the tinplate in a suitable electrolyte offers one possibility of preventing such staining by sulfur compounds. It is known that the resistance of tinplate to staining from protein-containing foodstuffs can be increased by subjecting the tinplate to an electrochemical aftertreatment in a sodium dichromate-containing electrolyte, in which treatment the tinplate is used as a cathode. In such conventional treatments an electrolyte is used which consists of an aqueous solution containing between 20 and 30 grams per liter of sodium dichromate while the electrolyte is maintained at a temperature between 71° and 93°C and its hydrogen-ion concentration at a value corresponding to a pH between 3.5 and 5.5. In this process, the electric current density measured at the cathode that is applied is at least 3.76 and at most 21.5 amperes per square decimeter. The duration of the treatment, that is, the period during which electrical charges are passed from the tinplate cathode to the electrolyte is between 1 and 3 seconds, during which period the desired amount of chromium and chromium oxide is deposited or plated on the tinplate.

As used herein, the term "current density" is to be understood to refer to the strength of the current per unit of cross-sectional area measured at the cathode and is expressed in terms of amperes per square decimeter. The total amount of electrical current that is consumed or the total electrical charge that is transferred to produce the specified chromium deposit on the tinplate is specified herein in terms of coulombs (amperes per second) per square decimeter. The total amount of electrical current that is consumed is the product of the current density and the period in seconds during which the current was passed. By use of the foregoing electrolyte and a temperature in the region of 50°C and a current density in the range between 0.2 and 0.5 ampere per square decimeter, the amount of current used thus being between 0.2 and 0.6 coulombs per square decimeter, between about 3 and 5 milligrams of chromium (as chromium and chromium oxide) per square meter will be deposited upon the tinplate in accordance with this conventional method. By increasing the current density to between 6.25 and 7.5 amperes per square decimeter and thereby the amount of current to between 9.5 and 11.25 coulombs per square decimeter, the amount of chromium and chromium oxide that is deposited on the tin plate can be increased to between 15 and 18 milligrams of chromium per square meter. By increasing the temperature of the electrolyte bath to about 80°C, chromium and chromium oxide in an amount equivalent to about 20 milligrams of chromium per square meter will be deposited on the tinplate when the density of the current is maintained at about 9.5 amperes per square decimeter, which corresponds to a total amount of 14 coulombs per square decimeter of current consumed.

The chromium coating deposited in accordance with this conventional method will have not only a reduced tendency to stain upon contact with sulfur compounds but will also be less susceptible to etching or corrosion when exposed to air or to acids or alkalies.

Despite such conventional electrochemical passivating treatments it has been found that the tin coating on such tinplate sheets dissolves upon contact with foodstuffs, unless the tinplate has been coated with an additional protective film of lacquer or resin. Furthermore such lacquer-coated tinplate is stained yellow at high temperatures which are normally used for soldering and sealing the container made of such tinplate. This staining is also referred to as scorch discoloration. Consequently the utility of such tinplate is also limited by the stability of the coating to heat.

A method is disclosed in U.S. Pat. No. 3,278,401 for improving the corrosion resistance of tin-containing surfaces and especially surfaces of tinplate on iron or steel substrates coated with iron-tin alloys by cathodically depositing chromium thereon. The electrolyte that is used in that method consists of an aqueous solution of a water-soluble chromate and sodium acetate or other water-soluble acetate. The sodium dichromate of that electrolyte was said to be replaceable by chromic acid (chromium trioxide CrO_3) and other water-soluble chromates. Only conventional weights of the coatings of chromium and chromium oxide were applied in this manner to the tin-coated iron or steel substrate. In this patent it was stated that the chromium deposit had good lacquer adhesion properties. Consequently it is evident that a film of lacquer was intended to be applied over the chromium coating to avoid the dissolving or migration of larger portions of tin from the thus-treated surface of the tinplate. The application of a film of lacquer increases considerably the cost of such tinplate. In that process the density of the electrical current that was applied was also limited and consequently the amount of chromium that could be deposited and the extent of the passivation that could be produced was also correspondingly restricted.

Another process is disclosed in U.S. Pat. No. 3,491,001 for the electrochemical treatment of tinplate to increase its corrosion resistance by means of a preliminary anodic treatment with a solution of ammonium or an alkali-metal carbonate followed by a cathodic treatment in an aqueous solution containing sodium dichromate having a hydrogen-ion concentration corresponding to a pH of less than 2.0. This treatment produced deposits of chromium having only the conventional weight or thickness which had the same disadvantages as the prior tinplate even though the treatment was said to provide an improved base for lacquer and other organinc coatings. Because of the high hydrogen-ion concentration, as represented by the low pH that is used in that treatment, the lining of the tank in which the electrochemical treatment is conducted is highly etched or corroded.

A process is disclosed in German Democratic Republic Pat. No. 45,536 in which corrosion and staining by sulfur compounds is said to be inhibited by the use of an electrolyte consisting of an aqueous solution of an alkali-metal dichromate having a hydrogen-ion concentration corresponding to a pH between 4.0 and 6.0. In accordance with that process deposits of chromium having only the normal weight or thickness which had been obtained in other processes and which have the same known disadvantages that other deposits having such weights could be obtained.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method and an electrolyte for the production of passivated tinplate that does not have the foregoing disadvantages, from which tinplate only relatively insignificant amounts of the tin coating are dissolved and which coatings also have a high stability to heat.

A further object of the present invention is to provide a method and electrolyte for passivating tinplate in which method the lining of the tank in which the electrochemical treatment is conducted is subjected to less destruction due to use.

The electrolyte that is used in the method of the present invention is distinguished principally from those disclosed heretofore in containing at least 5 and at most 10 grams per liter of an alkali-metal acetate together with 4 to 6, preferably 4.5 to 5.5, grams per liter of chromium trioxide (which is also referred to as chromic acid) the said electrolyte having a hydrogenion concentration corresponding to a pH between 4.0 and 5.0, and an electrical conductivity of at least 28,000, preferably at least 30,000, micromhos per centimeter at 50°C. The electrolyte contains preferably at least 20 and at most 25 grams per liter of an alkali-metal dichromate. Sodium acetate is an especially suitable alkali-metal acetate for use in the electrolyte.

The method of the present invention is distinguished principally from those disclosed heretofore in that the aftertreatment of the tinplate or sheets thereof that are to be used for the production of containers or cans, particularly those that are to be used for the packaging of foodstuffs, in the use of an electric current density measured at the cathode of at least 5.5 and at most 9.5 amperes per square decimeter, during a period of between 1 and 2 seconds, which corresponds to a consumption of electric current amounting to from 8 to 14 coulombs per square decimeter.

The aqueous electrolyte bath is preferably prepared by use of distilled or deionized water and is maintained during the electrochemical treatment at a temperature between 30° and 60°C, and preferably between 40° and 50°C.

By observing the foregoing parameters, deposits of chromium and chromium oxides amounting to between 25 and 35 milligrams of chromium per square meter upon tinplate can be obtained by use of relatively low electric current densities and without maintaining the electrolyte at higher temperatures.

Tinplate thus passivated in accordance with the method of the present invention has a higher resistance to staining by sulfur compounds and its susceptibility to atmospheric corrosion and corrosion in acidic and alkaline media is substantially reduced. The method of the present invention can be adapted for use in existing electrolytic tinplate manufacturing plants without requiring substantial alterations of the plant when the electrolyte of the present invention is used. A much smaller electric current density is required when the electrolyte of the present invention is used in place of the prior electrolyte that was used to deposit conventional coatings of normal thickness of chromium and chromium oxide to tinplate without changing the length of the period of treatment.

It is essential in order to increase the amount of deposited chromium and chromium oxide on tinplate in accordance with the method of the present invention that the electrical conductivity of the electrolyte be increased from the values in the region of 20,000 micromhos per centimeter that were previously used to values of preferably at least 30,000 micromhos per centimeter and by the use of chromium trioxide and the specified additional amount of alkali-metal acetate.

Tests extending for periods up to more than six months reveal that less than 60 milligrams of tin per kilogram of foodstuff dissolve or migrate in protein-containing foodstuffs that are packaged in containers made from tinplate passivated in accordance with the method of the present invention. Furthermore, such tinplate has a high resistance to corrosion, heat, and marbling.

The method and electrolyte of the present invention are illustrated and described further in the detailed description which follows.

DETAILED DESCRIPTION

In the following examples the passivating layers obtained consist of chromium, chromium trioxide and other chromium compounds, however, only the chromium content of the passivating layers is indicated.

EXAMPLE 1

A solution was prepared by dissolving the following substances in distilled water in the amounts specified:
25 grams per liter of sodium dichromate ($Na_2Cr_2O_7$),
5 grams per liter of chromium trioxide (CrO_3), and
10 grams per liter of sodium acetate (CH_3COONa).

The resulting solution had a hydrogen-ion concentration corresponding to a pH value of 4.6 and it had an electrical conductivity of 34,000 micromhos per centimeter at 50°C.

A continuous strip of tinplate both sides of which had been coated with tin having a width of 800 millimeters was connected to a source of electrical potential so that it could act as a cathode in an electrolytic reaction. This sheet was continuously passed between two pairs of anodes that were installed in a passivation tank containing the foregoing electrolyte, each anode having a length of 1500 millimeters. These anodes were so ar-

ranged that one pair of anodes was above and the other pair of anodes was below the tinplate sheet as it passed through the tank so that the sheet passed between the two pairs of anodes for a total distance of 3000 millimeters. The sheet was passed between the two pairs of anodes at a linear speed of 2 meters per second so that the period during which electrical charges were actually transferred from the cathode to the electrolyte was 1.5 seconds and the total surface area of the sheet, both sides of which were thus subjected to treatment, amounted to 480 square decimeters.

The temperature at which the electrolyte was maintained during the electrolysis was 50°C.

The total amount of electrical current per unit of surface area that was consumed by the tinplate sheet in this passivating tank was varied as specified in the following table. The total amounts of chromium in milligrams per square meter (rounded off to the nearest integer) that were thus deposited on both sides of the sheet are listed opposite the amount of the total amount of electrical current that was consumed in coulombs per unit of surface area, expressed as coulombs per square decimeter, in this table.

Total electrical current consumed coulombs per square decimeter	Chromium deposited, milligrams per square meter
0.15	4
0.30	6
0.65	8
1.30	10
1.95	11
3.22	14
4.0	16
8.0	25
14.0	35

COMPARATIVE EXAMPLE 1

In this example a solution corresponding essentially to that specified in Example 1 of U.S. Pat. No. 3,278,401 was used. This solution consisted of
25 grams per liter of sodium dichromate ($Na_2Cr_2O_7$), and
2.25 grams per liter of sodium acetate (CH_3COONa) dissolved in distilled water. It had a hydrogen-ion concentration corresponding to a pH of 5.3 and an electrical conductivity of 24,000 micromhos at 50°C. The continuous tinplate sheet that was used in Example 1 hereinbefore was then treated exactly as described in Example 1 while the temperature of the electrolyte was maintained at the same temperature that was used in Example 1, with the following results:

Total electrical current consumed coulombs per square decimeter	Chromium deposited milligrams per square meter
0.15	1
0.30	1–2
0.65	2–3
1.30	4
1.95	6
3.22	8
4.0	9

COMPARATIVE EXAMPLE 2

In this example a solution containing the maximum proportion of sodium acetate that is specified in the U.S. Pat. No. 3,278,401 was used. This solution consisted of
25 grams per liter of sodium dichromate ($Na_2Cr_2O_7$), and
3.75 grams per liter of sodium acetate (CH_3COONa) dissolved in distilled water. It had a hydrogen-ion concentration corresponding to a pH of 5.4 and an electrical conductivity of 26,000 micromhos at 50°C. The continuous tinplate sheet that was used in Example 1 hereinbefore was treated in exactly the same manner as described in Example 1, while the electrolyte was maintained at the same temperature that was specified in Example 1, with the following results:

Total electrical current consumed coulombs per square decimeter	Chromium deposited milligrams per square meter
0.15	1
0.30	1–2
0.65	3
1.30	4
1.95	6–7
3.22	8
4.0	9

As shown in Comparative Examples 1 and 2, it is not possible to obtain a higher lever of chromium passivity or chromium deposit because of the lower electrical conductivity of the electrolytes, which is apparent from a comparison of the current densities or charges transferred in terms of coulombs per square decimeter and the corresponding amounts of chromium deposited. The increase of the amount of chromium deposited in relation to the increasing amounts of electrical current consumed that were observed in Comparative Examples 1 and 2 would be obtained with conventional sodium dichromate electrolytes.

COMPARATIVE EXAMPLE 3

An electrolyte consisting of a solution of 25 grams per liter of sodium dichromate ($Na_2Cr_2O_7$) in distilled water having a hydrogen-ion concentration corresponding to a pH of 3.8 and an electrical conductivity of 22,700 micromhos per centimeter at 50°C was used in this example.

When the continuous sheet of tinplate that was used in Example 1 was treated with this solution in the same manner as described in Example 1 with the electrolyte at the same temperature that was maintained in Example 1, and with a current density of 0.21 ampere per square decimeter for a period of 1.5 seconds, corresponding to a total amount of electrical current consumed of 0.31 coulomb per square decimeter, the total amount of chromium deposited on both sides of the sheet was between 3 and 5 milligrams per square meter (conventional method).

When the current density was increased to 5.0 amperes per square decimeter, corresponding to a total amount of electrical current consumed of 7.5 coulombs per square decimeter, the total amount of chromium deposited on both sides of the sheet was between 14 and 16 milligrams per square meter.

Because of the low conductivity of the electrolyte of the comparative examples 1 to 3 it is not possible to use a higher current density, and because of the small amount of chromium deposited, a higher degree of passivity cannot be obtained with such electrolytes.

Example 1 together with comparative examples 1 to 3 demonstrate that the electrolyte that is used in the process of the present invention produces a substantially greater deposit of chromium in comparison with

known electrolytes at both low and high current densities. The passivating layers that are obtained with the electrolyte disclosed in U.S. Pat. No. 3,278,401 can also be obtained with electrolytes containing only an alkali-metal dichromate with no addition of sodium acetate.

The same results that are described in Example 1 and the Comparative Examples 1 to 3 are obtained when deionized water is used instead of distilled water.

EXAMPLE 2

To establish the amounts of tin, chromium, and iron that migrate into canned meats from tinplate coated with chromium passivating layers, pork and corned beef were packaged in cans formed from a commercial tinplate coated on both sides known as tin plate No. 57 = 0.75 lb/b.b., hardness Temper 3, the chromium passivating layers of which were equivalent to deposits of 4 and 25 milligrams of chromium per square meter, respectively. The results are listed in the following table in which I refers to the tinplate having a chromium layer equivalent to 4 milligrams per square meter and II refers to the tinplate having a chromium layer equivalent to 25 milligrams per square meter.

The amounts of the metals that were dissolved or migrated are tabulated in units of milligrams of the metal per kilogram of the meat. The amounts of metals that dissolved were determined at the following intervals, which are listed as the headings of the five columns of these tables under the respective letter designations:

A: Directly after sterilization
B: After storage for 1 month at room temperature
C: After storage for 2 months at room temperature
D: After storage for 1 month at 37°C.
E: After storage for 2 months at 37°C.

	Pork									
	A		B		C		D		E	
	I	II	I	II	I	II	I	II	I	II
Iron	15.3	8.0	17.0	8.5	21.0	10.5	24.0	12.0	24.5	14.0
Tin	6.0	5.0	9.0	5.5	13.0	8.0	17.0	8.5	19.0	10.0
Chromium	1.7	1.4	1.7	1.4	1.8	1.4	1.8	1.8	1.8	1.8

	Corned Beef									
	A		B		C		D		E	
	I	II	I	II	I	II	I	II	I	II
Iron	30.0	24.0	33.0	28.0	36.0	32.0	38.0	27.0	38.5	33.0
Tin	5.2	5.2	9.0	7.5	10.5	8.6	18.5	10.0	23.0	12.0
Chromium	1.4	1.7	1.6	1.8	1.7	1.8	1.8	1.8	1.8	1.8

The quantities of metals which migrated from cans made from tinplate in which evaporated milk having a butterfat content of 7.5% was packaged were also determined. The cans were made of the same tinplate as specified hereinbefore in connection with the canned meats that had a chromium passivating layer equivalent to 25 milligrams of chromium per square meter. The amounts of the respective metals that migrated into the evaporated milk packaged in such cans in milligrams per kilogram of the milk after storage at room temperature between 22° and 27°C for the specified periods are listed in the following table:

	Chromium	Tin	Iron
1 month	1.2	13.0	5.0
2 months	1.2	13.0	5.0
3 months	1.6	17.2	5.0
4 months	1.6	18.7	5.5
5 months	1.6	21.0	6.0
6 months	1.2	30.0	7.5

In this respect such highly passivated tinplate also exhibits high stability to marbling as well as high resistance to corrosion, even in sterilization experiments toward media that simulate foods which contain such substances as table salt, acetic acid, lactic acid, thioglycolic acid and mixtures thereof at temperatures of 121°C for periods between 30 and 60 minutes. They also have a greatly improved resistance to staining by sulfur compounds.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention.

Whaat is claimed as new and desired to be protected by Letters Patent is:

1. A method for treating a material having a tin-containing surface to passivate and improve the corrosion resistance of the said surface which comprises making the material a cathode in an aqueous hexavalent chromium electrolyte consisting essentially of an aqueous solution of an alkali-metal dichromate in an amount of at least 20 and at most 25 grams per liter, an alkali-metal acetate in an amount of at least 5 and at most 10 grams per liter, and chromium trioxide in an amount of at least 4 and at most 6 grams per liter, the said electrolyte having a hydrogen-ion concentration corresponding to a pH between 4.0 and 5.0 and an electrical conductivity of at least 28,000 micromhos per centimeter at a temperature of 50°C, and passing an electric current through the material and the electrolyte until an amount of chromium-containing film is deposited upon the said surface that is sufficient to improve the corrosion resistance of the said material.

2. A method as defined in claim **1** in which the electric current is passed through the material and the electrolyte for a period between 1 and 2 seconds and the said current has a density as measured at the cathode of at least 5.5 and at most 9.5 amperes per square decimeter, so that between 8 and 14 coulombs per square decimeter of current are consumed.

3. A method as defined in claim 2 in which the electrolyte is maintained at a temperature between 30° and 60°C.

4. A method as defined in claim 2 in which the electrolyte is maintained at a temperature between 40° and 50°C.

5. A method as defined in claim 2 in which the electric current is passed until the amount of chromium-containing film that is added to the material is equivalent to at least 25 milligrams of chromium per square meter of material.

6. A method as defined in claim 1 in which the alkali-metal acetate is sodium acetate.

7. An electrolyte for use in the method defined in claim 1 which consists essentially of an aqueous solution of an alkali-metal dichromate, an alkali-metal acetate in an amount of at least 5 and at most 10 grams per liter, and chromium trioxide in an amount of at least 4 and at most 6 grams per liter, said electrolyte having a hydrogen-ion concentration corresponding to a pH between 4.0 and 5.0 and an electrical conductivity of at least 28,000 micromhos per centimeter at a temperature of 50°C.

8. A method as defined in claim 1 in which the electrolyte consists essentially of an aqueous solution of an alkali-metal dichromate in an amount of at least 20 and at most 25 grams per liter, an alkali-metal acetate in an amount of at least 5 and at most 10 grams per liter, and chromium trioxide in an amount of at least 4.5 and at most 5.5 grams per liter, the said electrolyte having an electrical conductivity of at least 30,000 micromhos per centimeter at a temperature of 50°C.

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