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METHOD OF FORMING AN OXIDE COATING ON TIN

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This invention relates to the anodic chemical treatment of tin and tin alloys containing a high percentage of tin and articles made therefrom.

An object of our invention is the provision of a simple, direct and thoroughly practical process for chemically treating tin and tin alloys by anodic treatment in various electrolytes.

Another object of our invention is to provide a process for anodically treating the tin and tin alloy surfaces of articles, such as tin plate, wherein these surfaces shall be characterized by excellent heat absorption, high abrasion resistance, and continuity and uniformity of the treated tin surfaces.

Another object of our invention is the provision that the anodic heat absorbing film produced by the chemical process for treating the surface of tin or tin alloy, shall be adherent and sufficiently ductile in order that articles may be further fabricated by mechanical drawing, forming and/or bending operations.

Another object of our invention is the provision of chemically processing and anodically treating the surface of tin and tin alloy wherein the process is effective over a substantial range of temperature, electrolyte composition and concentration and current density so as to produce an effective anodic film on various types and grades of products having surfaces of tin and tin alloy. Other objects in part will be obvious and in part will be pointed out hereinafter.

As conducive to a clearer understanding of certain features of the invention, it may be noted at this point that tin articles having surfaces of tin or tin alloys shall also include tin plate. Hot dipped tin plate is generally considered to be steel base metal coated on its exterior surface with metallic tin, wherein intermediate to the tin and steel interface, an iron-tin alloy composition is formed. Tin plate may be formed by either the conventional method of hot dipping or electrolytically depositing the tin on the surface.

The coating weight of tin is usually specified as pounds of tin per basis box, or as grams of tin per square metre of tin plate. The conversion of weight per basis box to linear thickness depends on an assumed density which is compensated by the fact that in hot dip tin coats part of the coating is in the form of the tin-iron alloy component.

It is generally accepted that one pound per basis box is equivalent to 0.0000606 inch thick of tin on each face of the tin plate. One and one half pound tin plate is generally assumed

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to be about 0.0000909 inch thick. The proportional ratio between thickness and total weight of tin plate can be approximated from the relative proportions above mentioned, for hot dipped tin plate.

In the case of electrolytic tin plate thickness coating of 8 oz. to 10 oz. per basis box is generally acceptable; although some applications of tin plate may use less than one and one quarter pound but not less than one half pound per basis box.

In the present invention, the anodic chemical treatment of the tin plate is primarily directed toward tin plate having tin, greater than one and one quarter pound per basis box which would primarily be adaptable to hot dipped tin plate (4xxx); although the scope of the invention is also applicable to electrolytic tin plated articles.

The formation of oxide films of tin, as heretofore known, may be produced by converting tin into the oxide form by subjecting the tin under oxidizing conditions, such as air, at elevated temperatures. This process of subjecting tin to oxidizing conditions at elevated temperature has been conventionally used by the baking industry in converting the tin surfaces into oxides of tin by placing formed articles of tin plate in baking ovens at an elevated temperature of approximately 400 to 425° F. for a period of time of approximately 4 to 12 hours. This has been conventionally called the "burning in" or "burning out" process, wherein the baking pans acquire a color range from the interference films of light iridescent hues ranging in color from yellow, blue through greens, and subsequently a film having a degree of opacity may be obtained depending upon the chemical and physical characteristics of the tin plate surface in conjunction with variable atmospheric conditions during the "burning in" cycle.

It has been found that these oxide films possess wide variations in color characteristics; and it is highly desirable to eliminate these wide variations in order to produce bread of uniform and consistent crust color. In addition, the tin-iron alloy layer intermediate to the tin layer and the steel basis is brittle and less corrosion resistant than is the pure tin. Normally, the tin-iron alloy is increased with respect to the available tin layer by progressive "burning in" operation; and it is highly desirous to reduce the "burning in" time to about one hour. The baking industry finds it economically undesirable to subject the bread pans to a long period of "burning in"; because it ties up the baking ovens, baking pans,

as well as the personnel in a non-production operation, and also provides variable results. Also uniformity of crust color of bread is a definite sales factor; and a baker who can produce a uniform loaf of bread in the initial baking operation with a new baking pan set will increase his production capacity.

In addition, the adherence of oxides of tin by the conventional "burning in" method has been found to be very poor. Chemical as well as atmospheric factors which control the adherence of the oxides of tin are not well defined; and it is known that variations in the chemical and physical composition of the surface of the tin will produce variations in the adherence of the oxide film. Therefore, it is desirable to secure oxide film formation having heat absorption which is uniform and reproducible and at the same time to have a surface oxide film that will not tend to reflect the heat energy that impinges upon the surface of objects made of tin plate.

An outstanding object of the invention, accordingly, is the provision of an economical industrially practical process for anodically treating tin plated articles wherein work of widely varying quality with respect to chemical and physical tin surface compositions as well as shapes of manufactured articles, may be employed. In addition, the condition of the surface of the tin plate may be physically varied by mechanical operation; and under these conditions a uniform and a constant color oxide film, having excellent adherence and continuity, showing substantial reduction of spangling due to the breakdown of the large crystal growth on the tin surface, may be produced within a predetermined range of wholly practical conditions.

Referring now more particularly to the practice of this invention, the tin plate will normally have wide variations in the amount of tin on the surface, and will vary widely with respect to surface conditions, such as chemical composition, the presence of embedded organic foreign matter, porosity of the tin layer, and the crystalline structure of the tin surface. It is undesirable to have a heat reflecting exterior surface in a bread baking operation, and the conventional "burning in" process will reproduce oxides of tin corresponding to the initial surface condition.

The anodic chemical process of the present invention for treating tin surfaces will substantially reduce the heretofore mentioned objections; and in addition will substantially remove objectionable carbonaceous deposits within the porous tinplate, such as grease and oil, which will ultimately cause a non-uniform oxide layer to be formed on the surface of tin by the conventional "burning in" process.

In the chemical anodic treatment of tin plate, the articles or products of various shapes and configurations are electrolytically treated by using one or more of the articles or products as the anodes in an electrolytic bath.

The electrolytic bath contains at least one or more or combinations thereof of a complexing reagent consisting of substantial amounts of (1) polybasic organic acids, such as citric acid, picric acid, tartaric acid, oxalic acid, malic acid, maleic acid, and succinic acid; and (2) monobasic organic acids, such as acetic acid, lactic acid, propionic acid, benzene sulphonic acid, trichloracetic acid and salicylic acid; and (3) non-oxidizing inorganic acids, such as phosphoric acids, boric, molybdic, tungstic, and hydrofluoric acid; and (4) aqueous soluble salts, such as the alkali metal and/or alkaline earth salts of the above mentioned organic acids, or inorganic acids and other metallic salt compositions. It has been found that combinations of the complexing reagents in aqueous solution may be employed such as phosphoric acid, combined with citric acid, phosphoric acid combined with sodium phosphate; phosphoric acid combined with oxalic acid, acetic acid combined with sodium citrate, and sodium phosphate combined with sodium citrate. The scope of this invention shall not be limited to the chemical composition of the complexing reagents.

In the anodic treatment of tin plated articles and products in the electrolyte, it has been found advantageous to maintain current densities ranging from about 4 amps. per square foot to about 60 amps. per square foot of tin surfaces undergoing treatment together with a solution temperature of at least 50° C.; and usually more, up to the maximum temperature which falls below the boiling point of the solution so as not to cause excessive evaporation. Under the chemical conditions specified together with time of immersion, it is possible to obtain a uniform meta-stable tin oxide coating on tin plate having thickness ranging from about 3–5 micro inches to almost complete conversion of the free tin surface.

It is preferred to employ an electrolyte which by weight consists of at least 0.5% up to about 30% of the complexing reagents wherein the pH of the solution may be adjusted if necessary, with the corresponding acid or combination of other acids so that the pH range may vary from about a pH of 2 to a pH of about 8; and the remaining parts needed to form 100% by weight being substantially of water. It has been found that the anodic stanno-complexes of tin are more readily formed when the pH is within the range of about two and one-half (2½) to five (5).

One or more other tin plated articles such as tin formed baking pans are made the anode of the electrolytic solution and are subject to anodic treatment while maintaining a preferred solution bath temperature of about 80 to 98 degrees C. and a current density of about 20 to 40 amperes per square foot. The cathode may consist of shaped metallic compositions, such as stainless steel or the lead lined tank may be used as the cathode. Under such temperature conditions, the solution is found to remain stable to the extent that the complexing reagent is substantially retained in the bath with respect to weight percentage. The complexing reagent is not substantially chemically removed from the solution.

An uniform meta-stable oxide of tin may be imparted to the tin surface in a short interval of time. The time of immersion together with solution conditions are important factors with regard to the amount of meta stable tin oxide formed by the anodic treatment. It has been found that interference films of about 2 to 6 micro inches thick may be formed by anodic treatment in the electrolyte for an interval of time corresponding to a few seconds. In addition, it has been found that in a matter of minutes the entire tin layer can be converted into a meta stable oxide of tin.

As examples of other exceptionally stable, conductive and highly effective electrolyte solutions, and the related operating conditions which are employed for rapidly obtaining a uniform

continuous meta stable oxide of tin, mention is made of the following:

Treatment A

Electrolyte	Percent Total Weight of Bath
Disodium hydrogen phosphate, Na_2HPO_4	3–15
Ortho Phosphoric Acid, H_3PO_4 (85%)	2– 5

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 90–100° C.
Minimum current density ..... 15 amperes per square foot.
Time of immersion ..... 30–120 seconds.

Treatment B

Electrolyte	Percent Total Weight of Bath
Potassium Tartrate, $K_2C_4H_4O_6$	5–25
Tartaric Acid, $H_2C_4H_4O_6$	1– 3

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 80–100° C.
Minimum current density ..... 15 amperes per square foot.
Time of immersion ..... 30–120 seconds.

Treatment C

Electrolyte	Percent Total Weight of Bath
Citric Acid, $COOH.CH_2.C(OH)(COOH).CH_2.COOH$	5–20
Phosphoric Acid, H_3PO_4 (85%)	2– 4

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 80–100° C.
Minimum current density ..... 15 amperes per square foot.
Time of immersion ..... 30–120 seconds.

Treatment D

Electrolyte	Percent Total Weight of Bath
Tartaric Acid, $COOH.(CHOH)_2COOH$	5–50
Disodium Hydrogen Phosphate, Na_2HPO_4	5–30

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 80–100° C.
Minimum current density ..... 15 amperes per square foot.
Time of immersion ..... 30–120 seconds.

Treatment E

Electrolyte	Percent Total Weight of Bath
Sodium Tartrate, $Na_2C_4H_4O_6.2H_2O$	3–30
Disodium Hydrogen Phosphate, Na_2HPO_4	2–10

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 90–100° C.
Minimum current density ..... 15 amperes per square foot.
Time of immersion ..... 15–120 seconds.

Treatment F

Electrolyte	Percent Total Weight of Bath
Disodium hydrogen phospate, Na_2HPO_4	3–30

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 80–100° C.
Minimum current density ..... 20 amperes per square foot.
Time of immersion ..... 30–120 seconds.

Treatment G

Electrolyte	Percent Total Weight of Bath
Sodium Oxalate, $Na_2C_2O_4$	2–15
Phosphoric Acid, H_3PO_4 (85%)	3–10

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 70–100° C.
Minimum current density ..... 10 amperes per square foot.
Time of immersion ..... 60–250 seconds.

Treatment H

Electrolyte	Percent Total Weight of Bath
Magnesium Citrate, $Mg_3(C_6H_5O_7)_2.14H_2O$	3–10
Citric Acid	3– 5

Any remaining parts needed with the above to total 100 percent by weight, being substantially water.

Bath temperature ..... 90–100° C.
Minimum current density ..... 20 amperes per square foot.
Time of immersion ..... 60–150 seconds.

Particularly, an excellent meta stable oxide layer of tin was obtained on tin plate in the instance of Treatment A through Treatment H, inclusive. The scope of the invention should not be bound by any such quality of chemical composition, nor by the specific proportions of acids, salts and water given in the several illustrative examples of the treatment.

The treated tin plate articles are then removed from the electrolyte bath and rinsed with water in order to remove any occluded salts. The treated articles are then dried at slightly elevated temperature in order to remove the adherent water. The treated tin plate articles upon which the meta stable oxide of tin is deposited thereon are then subjected to an oxide conversion temperature condition whereby the meta stable oxide of tin is then converted at elevated temperatures, from about 190° C. to 230° C., to the stable form of the oxide of tin, primarily stannous-stannic oxide. This step in the process may be obtained by direct heat application to formulate the oxide conversion, although exposure to air or to any oxidizing condition will somewhat accelerate the oxide conversion.

The formation of the anionic stanno-complex of tin under electrolytic treatment will vary depending upon solution compositions and conditions. Since tin exhibits amphoteric properties, it has been noted that the meta stable oxide of tin may be formed under alkaline conditions; although the electrolytic step in the process is preferred under acid conditions (pH from 2½ to 5), successful results have been obtained under alkaline conditions. In addition it has been noted that the formation of the meta stable oxide of tin may be formed first by immersion in an alkaline media and then subsequently into an acid media or combinations thereof.

The complexing reagent forms the anionic stanno-complex which in turn is converted into the hydrate of stannous-stannic oxide. The hydrate is unstable in form and is then partially converted into the meta stable form of stannous-stannic oxide. The meta stable stannous-stannic oxide exhibits the interference films on the surface of tin, and when the thickness of the meta stable stannous-stannic oxide appears to approach seven (7) micro inches, opacity of the film begins to occur. By varying the time of immersion in the electrolytic bath, the blue-black meta stable stannous-stannic oxide is formed and at about 2 to 10 minutes immersion time under the aforementioned conditions it appears that the tin layer may be converted totally into the meta stable stannous-stannic oxide. Therefore, it is desirable to reduce the time of electrolytic immersion to about fifteen to ninety seconds in order to retain a relatively high percentage of free tin.

The time interval for electrolytic immersion will vary depending upon solution conditions. By reducing the current density and/or the temperature as well as the concentration of the complexing reagent, it is possible to increase substantially the time interval of immersion of the tin layer in the electrolytic bath. Therefore, the scope of the invention shall not be bound by the specific time interval of treatment specifically aforementioned.

The meta stable stannous-stannic oxide exhibits various transitional interference colors approaching the blue-black. The blue-black is then considered the end point of opacity and it has been found that the interference colors of red, purple, green and blue-green will upon subjecting the then treated meta stable stannous-stannic oxide to conversion conditions at elevated temperatures convert into a stable stannous-stannic oxide film structure exhibiting a uniform olive green color.

In examining a micro cross section of tin plate that has been subjected to the anodic treatment and temperature conversion, we have found that the stannous-stannic oxide layer may be varied in thickness ranging from a few micro inches to a thickness equivalent to the entire layer of available free tin. Micro cross section examination of a one and one half pound per basis box of untreated tin plate has revealed a thickness of free tin plus the tin-iron alloy layer of about 0.000090 inch. The tin-iron alloy layer on hot dipped tinplate will be approximately equivalent to about 0.000010 to 0.000015 inch thick. The amount of free tin on each surface of one and one half pound tin plate per basis box will approximate from 0.000060 to 0.000080 inch thick.

By allowing a sufficient time interval to elapse in the electrolytic immersion step, the free tin can be substantially converted into the meta stable form of stannous-stannic oxide. This appears to be undersirable and chemical control of the amount of meta stable stannous-stannic oxide is imperative. It has been found that a tin oxide layer of approximately 0.000007 to 0.000030 inch thick will exhibit the preferred uniformity of color as to heat absorption on the surface of the tin plate thereby retaining approximately 0.00004 to 0.00007 inch of free tin. Experimentally, it has been found that excellent bread baking was produced by converting substantially all of the free tin to tin oxide; although the corrosion resistance of the surface is slightly decreased.

The novel chemical treatment described in this process may be further accomplished by using a fused salt, such as disodium or dipotassium hydrogen phosphate dodecahydrate, as the electrolyte, or combinations thereof. One may consider this to be substantially an aqueous solution when the temperature of the electrolytic bath is within 80–100° C. We have found that satisfactory results can be obtained by holding the bath temperature to about 80–100° C., operating at a minimum current density of about 15 amperes per square foot, for time of immersion of about 20–90 seconds. When the current density was held at about 30 amperes per square foot, it was found that the voltage applied dropped to about 2 volts. In this invention, the term "complexing reagent" shall include a fused salt as described above.

In the conventional "burning in" process, both sides of the tin plate and/or articles and products formed therefrom, are converted into the oxide. It has been found highly desirable to achieve optimum heat transmission in a baking pan set, by having the outer surface of the tin plate heat absorbing and the inner surface, surface in contact with the bread, heat reflecting. This condition will provide a more uniform and efficient temperature gradient within the bread, and in addition provide the inner surface with a clean bright appearance thereby decreasing the baking cycle.

This novel design may be manufactured by placing a plurality, primarily two, of tinplate sheets back to back in contact with each other to form a tin plate structure. Paraffin, adhesives, waxes, oils, and other stop offs may be used between the contiguous surfaces of the respective tinplate sheets. The combined tinplate structure is then subjected to the anodic treatment, thereby producing individual sheets of tin plate having the heat absorbing opaque oxide layer on one side, and a bright reflective tin surface on the opposite side. Another novel method of treating one side of a sheet of tinplate is to place two sheets of tin plate back to back in contact with each other by first wetting the sheets in the electrolyte and then follow the process as previously described. The object of this procedure is to form a transparent tin oxide film on the inner bright contact surface, in order to substantially reduce the amount of tin oxide accumulated in the bread baking cycle. Transparent tin oxide on the inner bright surface of the tinplate may be acquired by subsequent immersion of the anodic treated tinplate in an alkaline media which will substantially reduce the formation of oxide during the conventional "burning in" cycle.

Prior to final temperature conversion step, the meta stable stannous-stannic oxide surface or the transparent oxide surface may be coated

with a stable high temperature organic bread releasing film, such as alkyl aryl silicones, polytetrafluoroethylene, polytrifluoromonochloroethylene and other high polymer film-forming organic substances and/or mixtures thereof, and then subjected to the temperature conversion step wherein independently but simultaneously the meta stable stannous-stannic oxide is converted to the stable stannous-stannic oxide and the organic film is cured. Excellent adhesion of the organic bread releasing films to the treated tin oxide films was obtained.

As many possible embodiments may be made of our invention and as many changes may be made in the embodiments hereinbefore set forth, it is to be understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

We claim:

1. In the formation of a heat absorbing tin oxide coating on a tin article, the process which comprises making the article the anode in an electrolyte solution, passing current through said electrolyte solution to form a film oxide coating on the article, removing the tin article from the electrolyte solution, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

2. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing a polybasic organic acid, passing current through said electrolyte to form a film oxide coating on the article, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

3. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing a monobasic organic acid, passing current through said electrolyte to form a film oxide coating on the article, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

4. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing a non-oxidizing inorganic acid, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

5. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing an aqueous soluble salt complexing reagent to form an anionic stanno-complex, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

6. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing a fused salt, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

7. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte, said electrolyte having a pH range from about 2 to 7, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

8. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

9. In the process of forming a tin oxide coating on the surface of a tin surface article by subjecting the tin article to an anodic electrolytic treatment in an electrolyte having a pH range from about 2 to 7, passing current through said electrolyte to form an oxide of tin, and removing the anodized tin article from the electrolyte, the improvement which comprises then subjecting the anodized article to a temperature range of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

10. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a polybasic organic acid said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

11. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an acidic electrolyte containing a polybasic organic acid, said electrolyte having a minimum pH of about 2, and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to a temperature from about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

12. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a non-oxidizing inorganic acid, and an inorganic salt in solution to form anionic

stanno-complexes, said electrolyte having a pH range from about 2 to 6, passing current through said electrolyte to form an oxide of tin, removing the anodized article from the electrolyte, and then subjecting the anodized article to a temperature of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

13. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a non-oxidizing inorganic acid and a metal organic salt in solution to form anionic stanno-complexes, said electrolyte having a pH range from about 2 to 7, passing current through said electrolyte to form an oxide of tin, removing the anodized article from the electrolyte, and then subjecting the anodized article to a temperature of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

14. In the process of forming a tin oxide coating on a tin surface article by subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of disodium hydrogen phosphate and phosphoric acid in solution to form anionic stanno-complexes, said electrolyte having a pH range from about 2 to 7, passing current through said electrolyte to form an oxide of tin, and removing the anodized article from the electrolyte, the improvement which comprises then subjecting the anodized article to a temperature of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

15. In the process of forming a tin oxide coating on a tin surface article by subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of disodium hydrogen phosphate in amount 3% to 15% by weight and phosphoric acid in amount 2% to 5% by weight in solution to form anionic stanno-complexes, said electrolyte having a pH range from about 2 to 7, passing current through said electrolyte to form an oxide of tin, and removing the anodized article from the electrolyte, the improvement which comprises then subjecting the anodized article to a temperature of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

16. In the process of forming a tin oxide coating on a tin surface article by subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of disodium hydrogen phosphate in amount 3% to 15% by weight and phosphoric acid in amount 2% to 5% by weight in solution to form anionic stanno-complexes, said electrolyte having a pH range from about 2 to 7, maintaining the current density at a value of at least 15 amperes per square foot and the electrolyte temperature at substantially 90° C. to about 100° C. to form an oxide of tin, and removing the anodized article from the electrolyte, the improvement which comprises then subjecting the anodized article to a temperature of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

17. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of potassium tartrate and tartaric acid to form an anionic stanno-complex, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

18. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of potassium tartrate and tartaric acid to form an anionic stanno-complex, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, maintaining the current density at a value of at least 15 amperes per square foot through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

19. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of potassium tartrate in amount of 5% to 25% by weight and tartaric acid in amount of 1% to 3% by weight to form an anionic stanno-complex, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, maintaining the current density at a value of at least 15 amperes per square foot through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated range of about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

20. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of citric acid and phosphoric acid to form an anionic stanno-complex, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to a temperature from about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

21. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing a complexing reagent consisting of citric acid in amount of 5% to 20% by weight and phosphoric acid in amount of 1% to 10% by weight to form an anionic stanno-complex, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to a temperature from about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

22. In the formation of a heat absorbing tin oxide coating on a tin surface article, the proc-

ess which comprises subjecting the tin article to anodic electrolytic treatment in an electrolyte containing a fused salt complexing reagent consisting of disodium hydrogen phosphate dodeca hydrate to form an anionic stanno-complex, passing current through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte, and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

23. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing citric acid and phosphoric acid, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current for 30 to 120 seconds through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to an elevated temperature from about 190° C. to 230° C. to convert said oxide to green oxide of tin.

24. In the formation of a heat absorbing tin oxide coating on a tin surface article, the process which comprises subjecting the tin article to an anodic electrolytic treatment in an electrolyte containing citric acid in amount of 5% to 20% by weight and phosphoric acid in amount of 2% to 4% by weight, said electrolyte having a pH range from about 2 to 7 and a temperature from about 60° C. to the boiling point of said electrolyte, passing current for 30 to 120 seconds through said electrolyte to form an oxide of tin, removing the anodized tin article from the electrolyte and then subjecting the anodized article to a temperature from about 190° C. to 230° C. to convert said oxide to the green oxide of tin.

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