

1

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METHOD FOR TREATING TIN SURFACES

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This invention relates to the treatment of tin or tin plate to develop a dull or colored surface for the purpose of modifying the surface characteristics of the tin to increase its heat absorbency and to decrease its heat reflectivity whereby the tin plate becomes more useful in the manufacture of baking utensils.

Until oxidation has been achieved by prior burning out of the tin on the outer walls of a baking pan or the like, the heat reflection from the surface of the tin is of such high order as to militate against the uniform and rapid baking of the dough or other like material contained in a baking pan. In order to secure the desired heat absorption and to minimize heat reflection, it has been customary to burn out the pan prior to use by exposure to high temperature for a time sufficient to develop a dull heat-absorbing, non-reflecting oxide coating. Such separate operation in advance of use of the pan for the purpose for which it was intended is not only costly and time-consuming but the temperature for burning out often exceeds the melting point of the tin with the result that fusion and loss of tin often results.

It is an object of this invention to produce a new and improved method for developing a permanent non-reflecting, heat absorbent surface on tin or tin plate and it is a related object to produce a new and improved baking tin, having a dull heat-absorbing color permanently formed in the surface thereof to permit immediate use of the pan for the purpose for which it was intended without prior burning out.

It has been found that such permanent and dull colored coating can be developed as an integral part of the tin or tin plate by electrolytic treatment wherein the tin plate or member formed thereof is immersed as the anode in an electrolytic bath containing an alkali metal hydroxide in combination with a water soluble chromate followed by thermal treatment at elevated temperature to develop the color in an attractive and uniform pattern over the entire surface of the metal.

The alkali metal hydroxide may be selected of sodium hydroxide, potassium hydroxide, lithium hydroxide or the like. While the amount of hydroxide can be varied, it is desirable to maintain a concentration of available hydroxide greater than 1 ounce per gallon of electrolyte, otherwise the surface will become pock-marked where electrolytic treatment is insufficient. More than 5 ounces of available hydroxide per gallon has been found to be undesirable because then the electrolyte functions as a solvent for the metallic tin whereby the tin is dissolved from the surface and occasionally areas of the base plate are exposed. Such exposed surfaces can rust or otherwise deteriorate in use. It is preferred to maintain the concentration of available alkali metal hydroxide within the ratio of 2 to 3½ ounces per gallon of electrolyte. The addition of alkali metal hydroxide to maintain the pH of the electrolyte between 11 and 14 has been found to be desirable.

As the water soluble chromate, use may be made of sodium bichromate, potassium bichromate, ammonium

2

bichromate or ammonium dichromate and the like. The concentration of chromate can be varied over a fairly wide range but the efficiency of the process is markedly reduced when the amount of chromate falls below 0.1 ounces per gallon of electrolyte. It is undesirable to make use of an amount of chromate in excess of the amount of sodium hydroxide. A very economical operation results in the use of an electrolyte containing 2 to 3 ounces sodium hydroxide to 1 to 2 ounces water soluble metallic chromate per gallon of electrolyte.

In the practice of this invention, use may be made of any suitable electrolytic conductor, such as a conductor formed of carbon, iron, steel or the like which function as the cathode immersed in the electrolyte.

The temperature of the bath is preferably maintained at about 180° F. At this temperature the desired coloration is rapidly developed uniformly throughout the surface of the material to be treated. It is undesirable to go far above 180° F. but bath temperatures as low as 120° F. may be used but with corresponding decrease in reaction rate and degree of coloration.

The current density in the bath may be varied over fairly wide limits depending upon the amount of current available and the concentrations of salts and hydroxide in the electrolyte. Under the conditions described, excellent results are secured with a current density of about 25 amperes per square foot of surface to be treated. At this amperage, a desired coloration develops within 2 to 5 minutes. When removed from the bath and rinsed to remove chemicals which might remain thereon after electrolytic treatment, the color formed on the tin surface may vary from green to red to brown generally arranged in striations throughout the surface. When the electrolytically treated tin surface is baked after rinsing, such as at a temperature ranging from 300–450° F. for a time ranging from at least one-half hour at the higher temperature to about three hours at the lower, or more, it has been found that a uniform drab color is formed throughout the surface. It has also been found that the electrolytic action raises the apparent melting point of the tin so that baking temperatures in excess of the melting point of tin may be used for more rapid baking out. Where color developed by the electrochemical reaction is absent in spots because of surface characteristics of the tin or because of scratches and the like, it has been found that the baking operation serves further to cause migration of the surface characteristics developed by the electrochemical reaction to such unreacted surface portions so that the final product will be substantially uniformly covered and protected throughout.

Upon close examination and testing of the colored surface produced in accordance with the practice of this invention, it appears that the developed color exists on the surface portion of the tin only and that such reacted surface enjoys higher abrasion resistance. The heat reflectivity of the surface is materially reduced even though the surface appears to retain some of its metallic luster.

By way of an example, an electrolytic bath may be formed of three ounces sodium hydroxide and one ounce sodium dichromate dissolved per gallon of aqueous solution. While the bath is heated to a temperature of about 180° F. a sheet of the tin or tin plate is immersed therein as the anode while passing a current density of 25 amperes per square foot of plate surface through the cell using a steel sheet as the cathode. After about 5 minutes, the sheet is removed and rinsed in water to remove electrolytic solutions and then baked for 30–45 minutes at a temperature of about 425° F. Under these conditions, the non-uniform coloring of red, green and

rown developed in the tin surface by the electrochemical reaction is converted into a fairly uniform gray-green color. Instead of baking at 425° F. the electrochemically treated tin may be heated for as many as 3 hours at 25-350° F.

By way of further example, use may be made of an electrolytic bath containing two ounces sodium hydroxide and one and one-half ounces potassium bichromate per gallon of water. The bath is heated to a temperature of about 160° F. and the tin member to be colored is immersed therein as the anode for about 3-5 minutes with a carbon cathode and a current density of about 35 amperes per square foot.

A metallic sheet treated in accordance with the practice of this invention may be formed into a suitable baking pan before or after heat treatment. It is preferred to lubricate the pan following electrolytic reaction because scratches and other tin surfaces exposed during fabrication appear to become colored perhaps by way of migration during the subsequent baking operation. It may be that the adjacent electrolytically treated surfaces beneficially affect the adjacent areas during baking or the spread of the protective coating may be in the form of a migration of the reaction products to cause the desired color to be developed upon such unreacted surfaces during baking. Whatever the reason, the final product in the form of a structure having a uniform dull, non-reflecting and heat-absorbing color permanently formed in the surface at temperatures which do not exceed the melting point of the tin so as to make the pan immediately available for use in the purpose for which it was intended.

It will be understood that changes may be made in the concentrations of compounds in the electrolytic bath and in the temperatures or current densities in the bath or electrochemical treatment and that the intensity of color developed may be increased or decreased by variation in reaction time and that other changes may be made without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In the method for treating tin to develop a permanent heat-absorbing, non-reflecting surface, the steps of electrochemically treating the tin surface while being submerged as the anode in an aqueous electrolytic bath containing 1-5 ounces per gallon of water soluble alkali metal hydroxide and 0.5-5 ounces per gallon of a water soluble chromate and then baking the electrochemically treated tin at a temperature above 300° F. until a uniform drab discoloration is formed over the treated surface.

2. In the method for treating tin to develop a permanent heat-absorbing, non-reflecting surface, the steps of electrochemically treating the tin surface while being submerged as the anode in an aqueous electrolytic bath containing 2-3½ ounces per gallon of a water soluble alkali metal hydroxide and a water soluble bichromate present in an amount within the range corresponding to an amount equal to that of the hydroxide as the upper limit to 0.5 ounce per gallon of electrolyte as the lower limit and then baking the electrochemically treated tin at a temperature above 300° F. until a uniform drab discoloration is formed over the treated surface.

3. In the method for treating tin to develop a permanent heat-absorbing, non-reflecting surface, the steps of electrochemically treating the tin surface while being submerged as the anode in an aqueous electrolytic bath containing from 1-5 ounces per gallon of a water soluble alkali metal hydroxide and a water soluble bichromate present in an amount within the range corresponding to an amount equal to that of the hydroxide as the upper limit to 0.5 ounce per gallon of electrolyte as the lower limit maintaining the electrolyte at a temperature of about 120-180° F., and passing a current therethrough at a density of about 35 amperes per square foot of surface to be treated and then baking the electrochemically treated tin at a temperature above 300° F. until a uniform drab discoloration is formed over the treated surface.

4. In the method for treating tin to develop a permanent heat-absorbing, non-reflecting surface, the steps of electrochemically treating the tin surface while being submerged as the anode in an aqueous electrolytic bath containing from 1-5 ounces per gallon of a water soluble alkali metal hydroxide and a water soluble bichromate present in an amount within the range corresponding to an amount equal to that of the hydroxide as the upper limit to 0.5 ounce per gallon of electrolyte as the lower limit, maintaining the electrolyte at a temperature of about 120-180° F., passing a current therethrough at a density of about 35 amperes per square foot of surface to be treated, and maintaining the electrochemical reaction for about 2-5 minutes and then baking the electrochemically treated tin at a temperature above 300° F. until a uniform drab discoloration is formed over the treated surface.

5. In the method for treating tin to develop a permanent heat-absorbing, non-reflecting surface, the steps of electrochemically treating the tin surface while being submerged as the anode in an aqueous electrolytic bath the solids of which consist essentially of 2-3½ ounces per gallon of a water soluble alkali metal hydroxide and a water soluble chromate salt present in an amount within the range corresponding to an amount equal to that of the hydroxide as the upper limit to 0.5 ounce per gallon of electrolyte as the lower limit, heating the electrolyte to a temperature within the range of 120-180° F., rinsing the electrochemically treated surface to remove electrolyte, and then baking the tin at a temperature within the range of 300-450° F. for a time ranging for about ½-3 hours.

6. Tin having a heat-absorbing, non-reflecting layer permanently formed in the surface thereof by the method claimed in claim 1.

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