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METHOD OF TINNING AND TINNED ARTICLES

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This invention relates to tinning, and with regard to certain more specific features, to a new tinning alloy bath, and to articles tinned with said alloy.

This application is in part a continuation of my application Serial No. 16,205, filed April 13, 1935.

Among the several objects of the invention may be noted the provision of a tinning alloy which, as a molten bath, has greater fluidity or lower surface tension, and which does not readily oxidize; the provision of a tinning bath which has a plastic range, whereby it need not be so closely controlled between temperature limits; the provision of a tinned article having a uniform, thin coating, notably free from lumps or other accumulations, in such manner that machined surfaces such as threads, etc., do not require to be re-machined after the tinning; the provision of a tinned article in which the coating is brighter and more corrosion-resistant; and the provision of a tinning alloy of the class described which is relatively economical to produce and use. Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly comprises the elements and combinations of elements, and features of structure and composition, which will be exemplified in the products hereinafter described, and the scope of the application of which will be indicated in the following claims.

The art of hot dip tinning has been in existence for a great many years. In such tinning, it is usually the custom to use pure molten tin, such as "straits" or "banka" tin. However, this procedure is subject to one great difficulty, in that the molten pure tin has a well-defined melting point, at which point the tin both melts and freezes, and unless precautions are taken to strip the excess tin in hot palm oil at a carefully controlled temperature, the product that is tinned will not be smooth but will be coated with lumps of tin. Such a lumpy coating is objectional in several respects. For example, in the case of machined articles, it is necessary after tinning to re-machine or chase the article in order to maintain the required tolerance.

In order to overcome this difficulty, it has been the custom in some establishments to add lead in amounts ranging from 0.50% to 50.00% to the tin in order to obtain a plastic temperature range between the melting and freezing points, thus giving the operator a chance to remove the excess tin. However, such added lead is objectionable in that it decreases the corrosion resistance of the tin coating, and it is further particularly detrimental in certain industries such as the food and dairy industries, where the lead is likely to be poisonous. Further, even with added lead in the tinning bath, it is necessary, in order to obtain a good coating, to maintain the tinning bath between relatively close temperature limits. If the bath is too cold, too much tin will adhere to the article, while if the bath is too hot, it will oxidize, forming a dross, and thereby producing a poor, uneven tinned surface.

The present invention comprises adding to a pure tin bath, which is free of intentionally added lead, a small amount of certain deoxidizing elements which improve the tinning bath in the following respects, and which also results in the production of a tinned coating on articles which is superior in numerous respects, to be described, to the tinned coating obtained with prior-art tinning compositions including both pure tin and lead-tin alloys. By such a procedure, the following beneficial results, among others, are noted:

A. The bath becomes more liquid. By this it is meant that the surface tension of the molten bath is decreased, while the fluidity of the bath is increased (that is to say, its viscosity is decreased), with the result that articles to be tinned may more readily be immersed and surplus alloy shaken therefrom.

B. The bath does not oxidize readily. This means that the formation of layers of dross on the surface of the molten tinning bath is minimized, and this causes the tin coating to be improved.

C. The range of temperatures at which the bath may be successfully kept for dip tinning purposes is immensely increased. This means that the temperature of the bath need not be so carefully controlled in order to obtain a good tin coating.

D. A plastic range is imparted to the tinning bath. By this is meant that there is a substantial range of temperatures between the melting point and the freezing point of the alloy, and this fact permits the operator to tin an article, and then have sufficient time in which to shake it to remove surplus tin before the cooling causes the coating to set.

E. Articles tinned with this bath have a coating which is thinner and much more uniform in thickness and completely free from lumps and the like. This is particularly advantageous in the case of articles machined to close tolerances, such as threads and the like. With the present invention, such articles do not require to be re-machined after being tinned.

F. Articles tinned in the bath of the invention

have a brighter coating, and one which more closely conforms to the original surface character of the article. By this is meant that if the article, for example, has an initially polished surface, the tinned surface will likewise appear to be polished; an initially rough cast surface will appear in the same manner after tinning.

G. The coating obtained in the present invention is more resistant to corrosion. This is because the alloy itself is more corrosion-resistant than pure tin, or than a tin-lead alloy, and in addition because the tinned surface is more uniform and free from porosity.

Among the elements suitable for adding to the pure tin, it has been found that phosphorous is most suitable. Phosphorus may be added to the molten tin bath in the form of phosphor-tin, a commercially available alloy containing about 5% of phosphorus and the remainder tin. Experiences have shown that even a minute amount of phosphorus has a beneficial effect in the tinning bath, but, from a practical standpoint, all of the advantages noted above do not accrue until the phosphorus is present in the bath to the extent of about 0.005%. This accordingly constitutes the lower limit of phosphorus from the commercial standpoint.

Experience has shown that the upper limit of phosphorus is about 0.2%. Above this phosphorus content, disadvantages accrue. For example, an alloy containing 1% phosphorus is disadvantageous because (*a*) considerable heavy yellow oxide dross continuously forms on the surface of the tinning bath, even though it be constantly removed, (*b*) the bath cannot be successfully operated at a temperature under 900° F., (*c*) the molten tinning bath has a corrosive influence on the pot, (*d*) the fluidity of the bath decreases, or its viscosity increases, to the point that it cannot readily be used, (*e*) the tinned coating on the articles is thick and rough, and not uniform, and (*f*) the tinned coating on articles is an unattractive dull gray color. Hence 0.2% may be considered as the upper limit of phosphorus from a commercial standpoint.

No elements other than the tin and phosphorus are intentionally present in the tinning bath. Of course it will be understood that the tin used in making up the bath, or the commercial phosphor-tin which may be used for adding the phosphorus to the bath, may and frequently do contain small percentages (scarcely ever exceeding 0.5% and infrequently exceeding 0.1%) of impurities, such as antimony, arsenic, lead, bismuth, copper, iron, silver, and sulphur, but these appear to have no deleterious effects when thus limited.

A practical, operating composition has been found to comprise a bath of molten pure tin which contains approximately 0.05% phosphorus. With such a composition, the bath may be successfully used at a temperature of about from 550° F. to 800° F. This compares with a maximum range of 20° F., permissible with a pure tin bath. This preferred bath forms substantially no oxide dross on its surface and exerts substantially no corrosive attack on the pot containing it. Its fluidity is much greater than that of a pure tin bath (that is to say, its viscosity is much lower than that of a pure tin bath).

Probably the most apparent advantages of such a bath, however, are found in the character of the articles tinned therewith. The coating so obtained is bright and shiny and of uniform thickness over the entire surface of the article, even when said surface is of highly complex varying character, such as in screw threads. Threaded articles with such a coating, for example, can readily be screwed into other similarly tinned threaded articles without chasing or re-cutting the threads. This is a distinct contrast to threaded articles tinned with pure tin where such chasing is absolutely necessary. Microscopic examination has shown that a tin coating of this composition is much thinner than the coating obtained with pure tin, and of a substantially uniform thickness over the entire surface of the tinned article. Microscopic examination of pure tin plate shows numerous thickness variations of as much as several hundred percent from region to region. The preferred composition, by contrast, shows substantially no variations in thickness in excess of about 20 per cent. With regard to the thickness of the coating obtained, a typical brass article, tinned with pure tin, showed a coating having a thickness of about 0.0059 inch, while a similar article tinned in exactly the same manner with the preferred alloy, has a coating with a thickness of about 0.0005 inch.

A further advantage of the coating obtained with the preferred alloy is that it is much more compact and free from pores than is the case with a pure tinned coating.

A still further advantage is that the tinning alloy of the present invention seems to reproduce the surface character of the tinned article. For example, if the article has a polished surface prior to tinning, the tinned coating obtained by the present invention likewise has a polished surface, or if the article has a matte surface the tinned article will likewise have a matte surface. With pure tin coatings, the coating is usually of a highly polished nature, regardless of the surface character of the article prior to tinning.

Experience has shown that articles tinned with this preferred composition have a resistance to corrosion that is largely in excess of the resistance of a pure tin or a tin-lead coating.

Among the other alloys of phosphorus and tin investigated, those found to embody all of the above advantages in greater or less degree, are those containing 0.005, 0.01, 0.015, 0.02, 0.025, 0.04, 0.065, 0.08, 0.10, and 0.15 per cent phosphorus.

The proper procedure to use in tinning articles with the bath of the present invention, for example, comprises (first) cleaning the article to free it of grease and the like, as, for example, in a degreasing solution or alkali cleaner; (second) fluxing the article in a bath of hydrochloric acid cut with zinc and to which has been added a little ammonium chloride; (third) dipping the article into the tinning bath; (fourth) dipping the article back into the flux; (fifth) returning the article to the tinning bath; (sixth) swinging or shaking the article in order to remove therefrom any surplus molten alloy; and (seventh) quenching the article in kerosene or the like.

A further advantage of the bath made in accordance with the present invention is that the phosphorous in the bath seems to have a beneficial cleaning or fluxing action on the article to be tinned, as it is found that the coating adheres much more quickly when the article is dipped into the bath.

A still further advantage is that a tinning bath made in accordance with the present invention does not seem to dissolve copper from the articles being tinned, as readily as pure tin, or tin-lead baths. With prior baths, this dissolving action took place constantly, and when the copper con-

tent of the bath increased up to about 7%, the bath became so sluggish that it had to be discarded. A bath made in accordance with the present invention does not appear readily to dissolve the copper in non-ferrous metals, and retains its fluidity and usefulness over extraordinarily long periods of time, even though it is in constant use. For example, a bath containing about 400 pounds of alloy has now been in substantially daily use in a commercial establishment, for a period of nine months, without any trouble whatsoever from dissolved copper.

The alloy of the present invention is suitable for tinning articles including (for example) brass, copper, bronze, and the like, and also ferrous alloys such as steel and cast iron.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As many changes could be made in carrying out the above compositions and processes without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. The method of tinning suitable metal articles which comprises dipping said articles in a molten bath of an alloy predominantly tin but including from about 0.005% to about 0.2% phosphorous.

2. The method of protecting the surfaces of metal articles from corrosion which comprises coating said surfaces with a thin layer of an alloy predominantly tin but including from about 0.005% to about 0.2% alloyed phosphorus.

3. An article of manufacture being the product of claim 1, consisting of a metal article having a thin protective coating of an alloy predominantly tin but including from about 0.005% to about 0.2% alloyed phosphorus.

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