Method of Electrodepositing a Tin-Bismuth Alloy and Compositions Therefor


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14 Claims

ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, the novel process of this invention for electroplating a tin-bismuth alloy plate may comprise immersing an article to be plated in an aqueous plating bath containing alkali metal stannate, free alkali metal hydroxide, and an alkali metal bismuthate; and electrodepositing a tin-bismuth alloy onto said article as cathode in said bath.

This invention relates to a novel technique for electroplating. More specifically it relates to a process for plating tin-bismuth alloys.

As is well known to those skilled in the art, metallic tin may be electrodeposited onto the surface of various basis metals including steel, brass, bronze, copper, etc. Typically, products bearing an electrodeposit of tin may find use because of the superior properties arising from the excellent resistance of tin to oxidation and/or the ability of tin to serve as a lubricant, as, e.g., on threads. Products which have been plated with tin, have been found to be satisfactory under normal conditions of use and/or storage; and when maintained under satisfactory, ambient conditions, including temperature typically above 18° C., the electrodeposited tin may retain its superior properties, including lubricity, for indefinitely long periods of time.

However it has been found, when materials bearing an electrodeposit of tin are maintained under conditions such that the ambient temperature falls below about 18° C., and particularly so when the temperature is below 18° C. for extended periods of time, that the tin metal is afflicted with tin pest.

The formation of tin pest on tin may be recognized firstly by the development of a dull lustre on a formerly shiny surface. Furthermore, especially after extended periods of time at temperatures below 18° C., tin pest, as formed in and on an electrodeposit of tin is observed as a fine nonadherent powder, and spots on the surface may have a corroded appearance. This loose tin powder, during its formation, separates from the surface of the basis metal and thereby loses its ability to protect that basis metal. As the tin pest continues to develop, the apparently loose, fine powder may form flakes which, in due course, may drop off from the basis metal thereby exposing the basis metal to corrosion and simultaneously removing therefrom the bulk of the tin plate. When this happens, the part becomes less attractive in appearance, loses its lubricity, and becomes much less able to withstand the effect of corrosion both before and after use.

It is an object of this invention to provide a process for electrodepositing a tin-containing plate. It is another object of this invention to electrodeposit a tin-bismuth alloy plate which is characterized by its high resistance to tin pest. Other objects will be apparent to those skilled in the art from inspection of the following description.

In accordance with certain of its aspects, the novel process of this invention for electrodepositing a tin-bismuth alloy plate may comprise immersing an article to be plated in an aqueous plating bath containing alkali metal stannate, free alkali metal hydroxide, and alkali metal bismuthate; and electrodepositing a tin-bismuth alloy onto said article as cathode in said bath.

The basis metal which may be plated in practice of this invention may be any suitable metal on which it is desired to produce an electrodeposited tin-containing plate. Typical basis metals which may be plated in accordance with the process of this invention may include steel, iron, brass, bronze, copper, etc. This invention may find particular use when used to electrodeposit a tin-containing plate onto the threads of, e.g., pipes or couplings, or when used to electrodeposit a tin-containing plate on the surface of, e.g., copper wire. The preferred basis metal with which the process of this invention may find use may be mild steel.

The aqueous plating baths used in the process of this invention may contain alkali metal stannate, e.g., sodium stannate or preferably potassium stannate.

The aqueous plating baths may contain alkali metal stannate in amount (expressed as grams per liter of tin contained therein) of 10—300 g./l., preferably 50—200 g./l., most preferably 150 g./l. Typically this may be attained when using the preferred potassium stannate by use of a bath containing about 375 g./l. of potassium stannate.

The aqueous baths may also contain free alkali metal hydroxide, typically potassium hydroxide or sodium hydroxide, most preferably potassium hydroxide. The bath may be made up by addition thereto of 5—35 g./l., preferably 15—25 g./l., most preferably 20 g./l. of alkali metal hydroxide, preferably potassium hydroxide.

It will be apparent that, when the aqueous bath is formed from and contains potassium stannate, the alkali metal hydroxide will preferably be potassium hydroxide; and that when the aqueous bath is formed from and contains sodium stannate, the alkali metal hydroxide will preferably be sodium hydroxide.

It is a feature of the novel aqueous baths of this invention that they contain an alkali metal bismuthate, preferably sodium bismuthate, potassium bismuthate, etc. Sodium bismuthate may be the most readily available alkali metal bismuthate and may be preferred.

In practice of the invention, bismuth metal may be added to the aqueous electroplating bath (in the form of alkali metal bismuthate) in amount of 0.05—1 g./l., preferably 0.2—0.75 g./l., say 0.6 g./l.

Thus the baths of this invention may contain the following components in solution:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin metal</td>
<td>10—200 50—290 150</td>
</tr>
<tr>
<td>Free alkali metal hydroxide</td>
<td>5—35 15—25 20</td>
</tr>
<tr>
<td>Bismuth metal</td>
<td>0.05—1.0 0.2—0.75 0.6</td>
</tr>
</tbody>
</table>

When the preferred components of this invention are employed, this may correspond to:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium stannate</td>
<td>175 200 295</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>5—35 15—25 20</td>
</tr>
<tr>
<td>Sodium bismuthate</td>
<td>0.06—1.4 0.25—1.0 0.75</td>
</tr>
</tbody>
</table>

Electrodeposition of tin-bismuth alloys from the bath so-prepared may be effected using either a soluble anode or an insoluble anode. If an insoluble anode be used, it may typically be of steel, preferably stainless steel. If a
soluble anode system is to be employed, the soluble anode may typically be tin, preferably commercial tin metal, or a high-speed tin alloy which may contain minor amounts of metals such as aluminum.

Electrodeposition of tin plate onto the cathode in such a system may preferably be effected at temperature of 60°C to the boiling point, e.g. 105°C, and preferably at about 95°C. Electroplating may be effected using a cathode current density of about 1 a.s.d to 40 a.s.d., preferably 8 a.s.d.

Elimination of the danger of tin pest from the electrodeposits formed in accordance with this invention may be effected by formation of an electrodeposited tin plate containing 0.1%–0.6%, say 0.2%, by weight of bismuth in the tin deposit. It is found that formation of the electrodeposited tin-bismuth alloy having a bismuth content within this range permits attainment of a desirable product characterized by a minimum occurrence of tin pest.

Electroplating in practice of this invention using the novel baths herein set forth may be effected by maintaining the article to be plated as cathode for 1–60 minutes, preferably 20 minutes. During this period of time, using the baths of this invention, it is readily possible to produce electrodeposits containing bismuth in the desired range in the tin deposit.

During operation in accordance with the novel process of this invention, the bismuth and tin content of the bath may preferably be maintained at the desired level, which is typically is one wherein the concentration of bismuth in the bath may be 50–1000, say 600 milligrams per liter which yields a ratio of bismuth to tin (each expressed as metal) of 0.001–0.006, preferably 0.002 in the plate. It will be noted that these ratios of bismuth to tin in the bath may yield deposits containing bismuth and tin wherein the bismuth may be present in amount of 0.1%–0.6%, typically 0.2%.

As is apparent, operation of the bath to produce the desired bismuth-tin alloy electroplate will deplete tin and bismuth from the bath. When a soluble tin anode is used, there will be substantially no depletion of tin from the bath except from that caused by dragout. Such additions of tin as may be required may be supplied by addition to the bath of appropriate amounts of alkali metal stannate. Depletion of the bismuth from the bath may be remedied by frequent addition to the bath of the alkali metal bismuthate hereinafter referred to, preferably at a rate of 0.005–0.006, say 0.002 gram of bismuth per ampere hour. Addition may be made at convenient intervals, e.g., every two hours or more often.

When the system is used with an insoluble anode, tin will also be depleted from the bath, and the tin depleted may be replenished by addition to the bath of appropriate amounts of alkali metal stannate typically in amount of 1.107 grams of tin per ampere hour. Maintenance of the level of bismuth in soluble anode systems may be effected by addition of the alkali metal bismuthate in the same manner as noted for the soluble anode systems.

Preferably, both the tin content and the bismuth content may be replenished by adding to the bath a maintenance composition containing alkali metal stannate and alkali metal bismuthate. Preferably, these two components may be present in a ratio equivalent to the bismuth: tin ratio of the desired electrodeposited. For example, these maintenance compositions may have a bismuth: tin ratio of 0.001–0.006:1 and preferably 0.002:1. The use of these maintenance compositions may permit operation of uniform tin-bismuth alloy plate during operation without the necessity of adjusting additions of the two separate components. These novel maintenance compositions are also highly convenient for the initial make-up of the plating bath.

In accordance with certain of its aspects, this invention may include a make-up and maintenance composition which comprises 10–300 parts, preferably 50–200 parts, 150 parts of tin metal (added as alkali metal stannate), and 0.05–1.0 part, preferably 0.2–0.75 part, say 0.6 part of bismuth metal (added as alkali metal bismuthate), preferably sodium bismuthate. This composition may be employed for make-up of a bath preferably when the bath contains a soluble anode. The tin loss from the bath is minimal when soluble anodes are used. The makeup and maintenance composition may also be used in connection with a bath containing insoluble anodes.

Practice of this invention permits consistent attainment, over an extended period of operation, of electrodeposits of bismuth-tin alloy containing 0.1%–0.6%, preferably 0.1%–0.3%, say 0.2%–0.3% bismuth, preferably 99.7%–99.9%, say 99.8% tin in novel electrodeposits may be particularly and unexpectedly characterized by its high resistance formation of tin pest after exposure for extended periods of time to temperatures considerably lower than 18°C.

Practice of this invention may be illustrated by referring to the following example, wherein all parts are by weight unless otherwise noted.

EXAMPLE 1

A 3-liter tin-bismuth alloy plating bath was made up to contain 0.75 g./l. sodium bismuthate (0.6 g./l. Bi), 22.5 g./l. KOH and 150 g./l. tin metal added as potassium stannate. The bath was maintained at 88°C, and steel panels were plated at a cathode current density of 6.45 ampers per square decimeter using steel anodes for a period of about one hour, after which a deposit having a thickness of 0.05 mm. of tin-bismuth alloy was obtained. The deposit had a bismuth content of 0.12–0.20%. The plated panels were incoated with grey tin by placing a small amount of powdered grey tin (tin pest) on the surface thereof and stored at a temperature between −15 and −18°C for six weeks. At the end of this time no grey tin (tin pest) developed on the deposit. Tin plated panels plated from identical baths which did not contain sodium bismuthate developed grey tin in objectionable quantities in only 24 hours storage under the same conditions.

From this example it may readily be seen that the panels plated in accordance with the novel process of this invention are outstandingly superior in resistance to formation of tin pest to plates plated according to typical prior art alkaline tin plating techniques.

Although this invention has been illustrated by reference to specific examples, numerous changes and modifications thereof which clearly fall within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. The method of electrodepositing a tin-bismuth alloy plate comprising immersing an article to be plated in an aqueous plating bath containing alkali metal stannate, free alkali metal hydroxide, and alkali metal bismuthate; and electrodepositing a tin-bismuth alloy plate onto said article as cathode in said bath.

2. The method as claimed in claim 1 of electrodepositing a tin-bismuth alloy plate wherein said alkali metal stannate is potassium stannate.

3. The method as claimed in claim 1 of electrodepositing a tin-bismuth alloy plate wherein said alkali metal bismuthate is sodium bismuthate.

4. The method as claimed in claim 1 of electrodepositing a tin-bismuth alloy plate wherein said alkali metal bismuthate is sodium bismuthate and wherein said alkali metal stannate is potassium stannate.

5. The method of electrodepositing a tin-bismuth alloy plate comprising immersing an article to be plated in an aqueous plating bath containing potassium stannate, free potassium hydroxide, and 0.05–1.0 g./l. of bismuth metal as sodium bismuthate; and electrodepositing a tin-bismuth alloy plate onto said article as cathode in said bath.
6. A novel bath for the electrodeposition of a tin-bismuth alloy plate which comprises an aqueous plating bath containing alkali metal stannate, free alkali metal hydroxide, and alkali metal bismuthate.

7. A novel bath as claimed in claim 6 for the electrodeposition of a tin-bismuth alloy plate wherein said alkali metal stannate is potassium stannate.

8. A novel bath as claimed in claim 6 for the electrodeposition of a tin-bismuth alloy plate wherein said alkali metal bismuthate is sodium bismuthate.

9. A novel bath for the electrodeposition of a tin-bismuth alloy plate which comprises an aqueous plating bath containing potassium stannate, free potassium hydroxide, and 0.05–1.0 gram per liter of sodium bismuthate expressed as bismuth metal.

10. A novel maintenance composition for aqueous tin-bismuth alloy electroplating baths which consists essentially of alkali metal bismuthate and alkali metal stannate.

11. A novel maintenance composition as claimed in claim 10 for aqueous tin-bismuth alloy electroplating baths wherein said alkali metal bismuthate is sodium bismuthate.

12. A novel maintenance composition for aqueous tin-bismuth alloy electroplating baths which consists essentially of 10–300 parts of tin metal as alkali metal stannate and 0.05–1.0 part of bismuth metal as alkali metal bismuthate.

13. A novel maintenance composition as claimed in claim 12 for aqueous tin-bismuth alloy electroplating baths wherein the ratio of bismuth to tin is 0.001–0.006:1.


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