United States Patent Office 3,360,446
Patented Dec. 26, 1967

3,360,446

ELECTRODEPOSITING A TIN-BISMUTH ALLOY AND ADDITIVES THEREFOR

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No Drawing. Filed May 8, 1964, Ser. No. 366,193
17 Claims. (Cl. 204—43)

ABSTRACT OF THE DISCLOSURE

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 alkaline plating bath containing alkali metal stannate, free alkali metal hydroxide, and hydroxy alkyl 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, typified by pipe couplings, 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 non-adherent powder. 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 which was intended to provide lubricity to the e.g. coupling. When this happens, the part becomes less attractive in appearance, less able to be joined with e.g. another coupling because of the decrease in lubricity, and 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. It is a further object of this invention to provide a process for constantly producing a uniform tin-bismuth electrodeposit. 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 hydroxy alkyl 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, 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 50–100 g./l., most preferably 90 g./l. Typically this may be attained when using the preferred potassium stannate by use of a bath containing 285 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 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 a hydroxy alkyl bismuthate, and preferably a polyhydroxy alkyl bismuthate. The bismuthate esters useful in practice of this invention may be formed by the reaction of a polyhydric alcohol with an alkali metal bismuthate, preferably sodium bismuthate.

Typical polyhydric alcohols which may be reacted may include the following: ethylene glycol, propylene glycol, glycerol, erythritol, arabitol, sorbitol, dulcitol, mannitol, cyclohexandiol, cyclohexantriol, cyclohexanpentol (quercitol), cyclohexanhexol (inositol).

Reaction between the alcohol and the bismuthate may typically proceed as illustratively set forth hereafter. Equimolecular proportions of sodium bismuthate and e.g. erythritol, mannitol, or inositol may be mixed together in a suitable vessel, with enough water to effect solution if necessary, adding the sodium bismuthate slowly and with constant stirring. When ethylene glycol, propylene glycol, or glycerol are used, the use of water as a solvent may be unnecessary. The resulting temperature of reaction must be carefully controlled (by use of ice or cold water bath) to 55° C.–80° C. as decomposition ensues at temperatures above 80° C. The reaction begins at about 55° C. and may be carried on up to about 80° C. Above 80° C. decomposition ensues and charring occurs.

When the reaction is complete the mixture may be allowed to cool to room temperature and a light tan or amber transparent fluid may be attained. This mixture may be extremely alkaline and an aqueous solution thereof (1 in 10) may have a pH of about 12. In order to prevent decomposition, neutralization of the resulting free sodium hydroxide may be effected immediately; and for this purpose it is preferred to use an organic acid.

Preferred acids which may be employed include soluble organic acids such as acetic, tartaric, citric, malic, and lactic acids. The strong mineral acids such as hydrochloric, nitric, and sulfuric acids are not preferred since a slight excess of these acids may be destructive to the product bismuth compound.

When neutralization has been effected by an organic acid to pH of approximately 7, the product may be poured into about 5 times its volume of ethyl alcohol. This may precipitate the bismuth compound, leaving a solution of the corresponding sodium salt, e.g. the acetate, tartrate, etc. of the acid employed for neutralization. The precipitate may be flocculent and dense and it may therefore be necessary after filtration to redissolve it in about three times its own weight of water and again precipitate it with ethyl alcohol as above. It is desirable to again dissolve the second precipitate thus formed in water and form a third precipitate by treatment with ethyl alcohol.

The compound thus purified, may then be dried in a suitable oven at 100° C. and reduced to a fine powder. In powder form, the compounds may typically be pale yellow or brown heavy powders which when drum-dried may consist of thin, transparent amber or brown scales. They are relatively stable in air and have characteristic odors.

Illustrative compounds prepared by the reaction of polyhydric alcohol and bismuthate may have the following composition expressed as percent by weight:

Dihydroxypropyl bimuthate, $C_3H_5(OH)_2BiO_3$:

	Percent
Bismuth	62.8
Carbon	10.8
Oxygen	24.1
Hydrogen	2.1

Trihydroxybutyl bismuthate, $C_4H_6(OH)_3BiO_3$:

Bismuth	57.7
Carbon	13.2
Oxygen	26.5
Hydrogen	2.4

Pentahydroxyhexyl bismuthate, $C_6H_8(OH)_5BiO_3$:

Bismuth	49.5
Carbon	17.1
Oxygen	30.3
Hydrogen	3.0

Pentahydroxycyclohexyl bismuthate, $C_6H_6(OH)_5BiO_3$:

Bismuth	49.7
Carbon	17.1
Oxygen	30.3
Hydrogen	2.6

These compounds may be very soluble in water and glycerin, but insoluble in alcohol, acetone, or ether. The preferred compound may be pentahydroxyhexyl bismuthate prepared from sorbitol and sodium bismuthate.

In practice of the invention, the bismuthate ester may be added to the aqueous electroplating bath in an amount (expressed in term of bismuth metal content therein) of 0.05–1.5 g./l., preferably 0.4–1 g./l., say 0.5 g./l.

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

Component	Concentration, grams per liter		
	Broad	Narrow	Preferred
Alkali metal stannate [1]	10–300	50–100	90
Free alkali metal hydroxide	5–35	15–25	20
Bismuthate ester [2]	0.05–1.5	0.1–0.5	0.3

[1] Expressed in terms of tin metal content.
[2] Expressed in terms of bismuth metal content.

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 most preferably effected by formation of an electrodeposited tin plate containing 0.1%–0.3%, 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 equilibrated baths of this invention, i.e. baths which have been used sufficiently long to be past their break-in period, it is readily possible to produce electrodeposits containing bismuth in the desired range within the tin deposit. It is a particular characteristic of the novel baths of this invention that after the initial break-in period, they may be used substantially indefinitely e.g. for periods in excess of 125 ampere hours per liter; and during this time the product plate attained will be substantially uniform.

It is also a particular feature of the novel baths of this invention that they have a short break-in period. Typically these baths may be found to yield the desired product alloy electroplate typically after a break-in period of as little as 5 ampere hours per liter and frequently after only 4 ampere hours per liter. Thereafter the process permits production of the noted plate for a substantially indefinitely long time.

During operation in accordance with the novel process of this invention, the bismuth and tin content of the bath may readily be maintained at the desired level, which typically is one wherein the concentration of bismuth in the bath may be 50–150, say 100 milligrams per liter which yields a ratio of bismuth to tin (each expressed as metal) of 0.001–0.006, preferably 0.003 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 0.3%.

The break-in period, which typically may be 4–5 ampere hours per liter may be decreased substantially to zero by the use, in the break-in period, of ratios of bismuth to tin which are about 50% of the corresponding values hereinbefore set forth for use during normal operation. Thus during this period, the bismuth content of the bath may be 0.025–0.75, preferably 0.05–0.2, say 0.10 g./l.

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 stannates. Depletion of the bismuth from the bath may be remedied by frequent addition to the bath of the bismuthate ester hereinbefore referred to, preferably pentahydroxyhexyl bismuthate at rate of 0.0005–0.005, say 0.003 gram of bismuth per ampere hour. Addition may be made at convenient intervals e.g. every two hours.

When the system is used with an insoluble anode, tin may be replenished by addition to the bath of appropriate

amounts of alkali metal stannate in amount of 1.107 grams of tin per ampere hour. In this case, 1.04 grams per ampere hour of potassium hydroxide (or an equivalent quantity of sodium hydroxide when the bath contains sodium) must be neutralized by appropriate methods known to those skilled in the art.

Maintenance of the level of bismuth in insoluble anode systems may be effected by addition of the bismuthate ester in the same manner as noted for the soluble anode systems.

It is a particular feature of this invention that when the process for electrodepositing a bismuth-tin alloy is conducted in a system (and particularly when the system is a potassium stannate system) using an insoluble or inert anode that the tin content of the bath may be maintained or replenished by addition to the bath of a hydrous tin oxide sol such as that disclosed in my copending application Ser. No. 366,146 entiled Novel Technique, filed simultaneously herewith. These alkaline tin oxide sols which are characterized by their substantially complete convertibility to stannate when in contact with solutions containing 5–100 g./l. of potassium hydroxide at temperature of 50° C.–100° C. may be prepared by the process which comprises reacting at temperature less than 75° C., an alkali metal stannate in an aqueous solution with acid to a final pH of less than about 6 thereby precipitating hydrous stannic oxide, separating said hydrous stannic oxide from said aqueous medium, washing said hydrous stannic oxide thereby removing water-soluble ions, peptizing said hydrous stannic oxide with peptizing agent selected from the group consisting of potassium hydroxide and potassium stannate thereby forming an alkaline tin oxide sol, maintaining the molar ratio of potassium to tin in the final sol of 0.1–1.5, and maintaining said hydrous stannic oxide at temperature below 75° C. prior to said peptizing.

Typically such a convertible tin sol may be prepared by heating to 49° C., a solution containing 1000 grams of potassium stannate dissolved in two liters of water. During heating, 700 grams of sodium bicarbonate may be added thereto in small increments. During the addition, the solution may be stirred and the temperature maintained at 49° C.±3° C. The precipitate which formed may be filtered and washed with 500 ml. of cold water. After washing, the precipitate may be suspended in 1.5 liters of water and 120 ml. of glacial acetic acid added to bring the pH to about 5. The precipitate may again be filtered and washed with water. It may then be mixed with 200 grams of solid potassium stannate, whereupon a fluid, clear, slightly amber alkaline tin oxide sol may be obtained. The product sol may weigh 1465 grams, have a specific gravity of 1.63, and contain 28.6% by weight tin.

It is a particular feature of this invention in accordance with certain of its aspects, that the novel baths of this invention may be made up and maintained by the use of a mixture (i.e. solution) of the hydroxy alkyl bismuthate esters and the alkaline tin oxide sol. A typical make-up composition may include alkaline tin oxide sol in amounts (expressed in terms of tin metal of 100 g./l.–700 g./l., say 300 g./l.; and hydroxy alkyl bismuthate ester (expressed in terms of bismuth metal) in amount of 0.1 g./l.–3.5 g./l., say 0.9 g./l. These bismuth- and tin-containing compositions may be used in the form of an aqueous composition formed by mixing the reaction product of the polyhydric alcohol and the bismuthate directly with the aqueous composition containing the alkaline tin oxide sol.

A typical make-up and maintenance composition may thus include 0.1–3.5 part, say 0.9 part of pentahydroxyhexyl bismuthate (expressed in terms of bismuth metal) and 100–700, say 300 parts of alkaline tin oxide sol (expressed in terms of tin metal). This composition may be used as a maintenance composition preferably when the bath contains an insoluble anode.

In accordance with certain of its other aspects, the invention may include a make-up and maintenance composition which comprises 10–300 parts, preferably 50–100 parts, say 90 parts of alkali metal stannate (expressed as tin metal) and 0.05–1.5 parts, preferably 0.4–1 part, say 0.5 part of hydroxy alkyl bismuthate (expressed as bismuth metal) preferably pentahydroxyhexyl 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 make-up 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%, typically 0.2% bismuth and 99.4%–99.9%, preferably 99.7%–99.9%, typically 99.8% tin. This novel electrodeposit may be particularly and unexpectedly characterized by its high resistance to formation of tin pest after exposure for extended periods of time to temperatures considerably lower than 18° C.

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

Example 1

In this example, dihydroxypropyl bismuthate may be prepared by reacting glycerol and sodium bismuthate. The charge materials may be mixed together in a suitable vessel, with stirring as the solid sodium bismuthate is added to the liquid glycerol. The temperature of reaction may be carefully controlled by the use of a cold water bath so that during the reaction the temperature may be maintained at 55° C.–60° C. Reaction may proceed over 30 minutes and on cooling the mixture, a light, amber, transparent fluid may be noted. Neutralization may be effected with citric acid to a pH of approximately 7 by addition of the solid acid with agitation. The entire reaction mixture may then be poured into 5 times its volume of ethyl alcohol thereby precipitating the product bismuth ester dihydroxypropyl bismuthate. The precipitate may be separated by filtration and dissolved by 3 times its weight of water. Precipitation may then be effected by addition by 3 times the volume of ethyl alcohol. The precipitate may be separated by filtration, dried at 100° C., and reduced to a fine powder.

Example 2

The compound pentahydroxyhexyl bismuthate was prepared in the same manner as the product of Example 1, except that an equivalent amount of sorbitol was substituted for the glycerol.

Example 3

Two identical electroplating baths were made up each containing 283 g./l. potassium stannate and 20 g./l. potassium hydroxide. To the first bath was added the composition prepared in accordance with Example 1, in amount of 0.3 g./l., which yielded a ratio of bismuth to tin (expressed in terms of metal) of 0.002. To the second bath was added 0.4 gram of the composition prepared in accordance with Example 2 which yielded a ratio of 0.002 of bismuth to tin.

Eighteen steel cathodes, each 0.1 x 2.5 x 15 cm. were plated successively in each bath at 6 amperes per square decimeter (a.s.d.) for 30 minutes at 77° C. The electrodeposit on each cathode was analyzed and the analysis, in terms of percent of bismuth in the tin deposit, was plotted as a function of the ampere hours per liter put through the bath.

After the initial break-in period, up to about 4.4 ampere hours per liter, the bath containing the composition of Example 1 continuously produced a deposit uniformly containing bismuth in the range of 0.25%–0.3%. After the bath had been in operation for about 6.3 ampere hours per liter, the electrodeposit formed contained about

0.25% bismuth, which level was maintained essentially constant substantially indefinitely until the test terminated at 12.5 ampere hours per liter.

Example 4

The bath containing the composition of Example 2 was found to be substantially identical in performance to the bath containing the composition of Example 1. The bath of Example 2 permitted attainment of an electrodeposit containing 0.3% bismuth after about 5 ampere hours per liter and thereafter performed substantially identically to the bath of Example 1.

Example 5

In this example, which was a life test illustrating the highly superior results of the novel process of this invention, a bath was made up identical to that of Example 3. The bismuth content of this solution was established by the addition to the solution of pentahydroxyhexyl bismuthate at intervals during electroplating. The bismuth and the tin content were maintained by addition to the bath of an aqueous composition containing 500 g./l. of tin (as alkaline tin oxide sol) and 1 g./l. of bismuth (as pentahydroxyhexyl bismuthate). The additions were made in accordance with the ampere hours per liter passed through the bath—1.107 grams of tin being added per ampere hour passed through the solution; this addition was made at intervals of approximately two hours.

Steel plates identical to those used in Example 3 were electroplated successively in this bath over the life of the test. It was found that, in this example, after the initial break-in period, the percent bismuth in the tin deposit was maintained substantially constant at about 0.2% bismuth in the plate to the end of the test at 119 ampere hours per liter; and from the slope of the curve (i.e. horizontal), it was apparent that the bath could be used for an indefinitely long time to give a bismuth-tin alloy electrodeposit having fixed, predetermined composition.

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 alkaline plating bath containing alkali metal stannate, in amount of 10–300 grams per liter (expressed in terms of contained tin), free alkali metal hydroxide, and hydroxy alkyl bismuthate; and electrodepositing a tin-bismuth alloy plate onto said article as cathode in said bath.

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

3. The method of electrodepositing a tin-bismuth alloy plate as claimed in claim 1 wherein said hydroxy alkyl bismuthate is a polyhydroxy alkyl bismuthate.

4. The method of electrodepositing a tin-bismuth alloy plate as claimed in claim 1 wherein said hydroxy alkyl bismuthate is pentahydroxyhexyl bismuthate.

5. The method of electrodepositing a tin-bismuth alloy plate as claimed in claim 1 wherein said hydroxy alkyl bismuthate is present in concentration of 0.05–1.5 grams per liter expressed as bismuth metal.

6. The method of electrodepositing a tin-bismuth alloy plate comprising immersing an article to be plated in an aqueous alkaline plating bath containing potassium stannate in amount of 10–300 grams per liter (expressed in terms of contained tin), free potassium hydroxide, and 0.05–1.5 g./l. of hydroxy alkyl bismuthate expressed as bismuth metal; and electrodepositing a tin-bismuth alloy plate onto said article as cathode in said bath.

7. The method of electrodepositing a tin-bismuth alloy plate as claimed in claim 6 wherein said hydroxy alkyl bismuthate is pentahydroxyhexyl bismuthate.

8. A novel bath for the electrodeposition of a tin-bismuth alloy plate which comprises an aqueous alkaline plating bath containing alkali metal stannate in amount of 10–300 grams per liter (expressed in terms of contained tin), free alkali metal hydroxide, and hydroxy alkyl bismuthate.

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

10. A novel bath for the electrodeposition of a tin-bismuth alloy plate as claimed in claim 8 wherein said hydroxy alkyl bismuthate is pentahydroxyhexyl bismuthate.

11. A novel bath for the electrodeposition of a tin-bismuth alloy plate which comprises an aqueous alkaline plating bath containing potassium stannate in amount of 10–300 grams per liter (expressed in terms of contained tin), free potassium hydroxide, and 0.05–1.5 grams per liter of a hydroxy alkyl bismuthate expressed as bismuth metal.

12. A novel composition for make-up and maintenance of aqueous electroplating baths for deposition of a tin-bismuth alloy plate consisting essentially of a hydroxy alkyl bismuthate and an alkaline tin oxide sol.

13. A novel composition for make-up and maintenance of aqueous electroplating baths for deposition of a tin-bismuth alloy plate as claimed in claim 12 wherein said hydroxy alkyl bismuthate is pentahydrohexyl bismuthate.

14. A novel composition for make-up and maintenance of aqueous electroplating baths for deposition of a tin-bismuth alloy plate consisting essentially of 0.1–3.5 parts of hydroxy alkyl bismuthate (expressed in terms of bismuth metal) and 100–700 parts of an alkaline tin sol (expressed in terms of tin metal).

15. A novel composition for make-up and maintenance of aqueous electroplating baths for deposition of a tin-bismuth alloy plate consisting essentially of alkali metal stannate and hydroxy alkyl bismuthate.

16. A novel composition for make-up and maintenance of aqueous alkaline electroplating baths for deposition of a tin-bismuth alloy plate consisting essentially of 10–300 parts of alkali metal stannate and 0.05–1.5 parts of hydroxy alkyl bismuthate (expressed as bismuth metal).

17. A novel composition for make-up and maintenance of aqueous alkaline electroplating baths for deposition of a tin-bismuth alloy plate consisting essentially of 50–100 parts of alkali metal stannate and 0.05–1.5 parts of pentahydroxyhexyl bismuthate (expressed as bismuth metal).

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