

[54] ELECTROLYTE FOR AND METHOD OF BRIGHT ELECTROPLATING OF TIN-LEAD ALLOY

[75] Inventors: Nobuyasu Dohi; Mikio Kamon, both of Kobe, Japan

[73] Assignee: Hyogo Prefectural Government, Kobe, Japan

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[58] Field of Search..... 204/43 S, 53, 54 R

[56]

References Cited

UNITED STATES PATENTS

2,598,486	5/1952	Andrews .....	204/54 R
2,633,450	3/1953	Andrews .....	204/54 R
3,661,730	5/1972	Nishihara.....	204/43 S

FOREIGN PATENTS OR APPLICATIONS

1,030,209	5/1966	United Kingdom.....	204/54 R
1,151,460	5/1969	United Kingdom .....	204/43 S

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Ernest G. Montague; Karl F. Ross; Herbert Dubno

[57]

ABSTRACT

A method of and an electrolyte for the bright electroplating tin-lead alloys which comprises using as the plating solution a mixture which contains phenolsulfonates or cresolsulfonates of divalent tin and lead, with the "reaction products of aliphatic aldehydes with aromatic primary amines," and acetaldehyde.

5 Claims, No Drawings

## ELECTROLYTE FOR AND METHOD OF BRIGHT ELECTROPLATING OF TIN-LEAD ALLOY

This application is a continuation-in-part application of Ser. No. 199,396 filed Nov. 15, 1971, now abandoned.

### SUMMARY OF THE INVENTION

This invention relates to a method of and an electrolyte for the bright electroplating tin-lead, which is characterized by using phenolsulfonates or cresolsulfonates of divalent tin and lead as the commonly soluble complex salts, and by using reaction products of aliphatic aldehydes with aromatic primary amines and acetaldehyde as additives to the solution containing the above complex salts. It is an object to prevent the occurrence of public pollution by using less poisonous salts than borofluoric acid and its salts of tin and lead which are now used for the electroplating of tin-lead alloy. It is also an object to provide a bright electrodeposit of a tin-lead alloy wherein the ratio of metal components in the plating solution is more nearly equal to that in the deposit than in case of a plating solution using salts of borofluoric acid, in the range of working condition and with a stable electrolyte.

### DETAILED DESCRIPTION OF THE INVENTION

This invention is characterized by providing tin-lead alloy electrodeposits having excellent brightness and a desired optional composition without the use of strongly poisonous chemicals such as salts of borofluoric acid, which have been used heretofore to obtain electrodeposition of tin-lead alloys but are not desirable from the viewpoint of both environmental sanitation and protection against public endangerment. In the conventional method of bright electroplating of a tin-lead alloy onto a substrate, where salts of borofluoric acid are used together, and when various additives necessary for bright plating are used, the ratio of tin to lead is higher in the deposit than in the plating solution, in the range of usual working conditions, because the electrical potential of lead in the solution is very much higher than that of tin. It has been found that the brighter the deposit is, the stronger this tendency is. However, in the method of bright electroplating of tin-lead alloy, using phenolsulfonates or cresolsulfonates, and using as an additive, reaction products of aliphatic aldehydes with aromatic primary amines, and acetaldehyde, and supplementary additives as mentioned in the following Examples, the deposit of the desired composition can be obtained in the range of usual working conditions only by controlling the concentration ratio of metals in the plating solution, without regard to the amount of additives, temperature, current density, state of agitation of the solution, degree of brightness of the deposit, and other variables, because the electric potentials of tin and lead in the solution are made nearly equal.

It is not essential in this invention to use the combination of the surface active agents as described in the examples, because phenolsulfonic acid and cresolsulfonic acid per se, function as surface active agents. They, therefore, can be replaced by other surface active agents which are expected to have similar effect. However, when the combination of phenolsulfonate or cresolsulfonate of divalent tin and lead with the reaction products of aliphatic aldehydes with aromatic primary

amines is changed, the above-described effects, mainly, protection against public pollution, equality of the metal composition in the solution to that in the bright deposit over the wide range of working conditions and so on, can not be expected.

The reaction products of aliphatic aldehydes with aromatic primary amines were prepared by reacting one mol of an aromatic primary amine with one or more mols of an aliphatic aldehyde, e.g., as disclosed in British Pat. No. 1,030,209.

Phenolsulfonic acid and cresolsulfonic acid prevent divalent tin in the plating solution from being oxidized by atmospheric oxygen to tetravalent tin, because they function as antioxidants. Therefore, they prevent the formation of tetravalent-tin salt precipitates which have poor solubility, and thus ensure clarity of the solution which is especially desirable in bright plating.

### EXAMPLE 1

Divalent tin (used in the form of stannous phenolsulfonate)	15 g/l
Lead (used in the form of lead phenolsulfonate)	10 g/l
Free phenolsulfonic acid	100 g/l
Brightening agent (20% by weight solution of the precipitate which was extracted with isopropyl alcohol after the reaction of 5 mols of acetaldehyde with 1 mol o-toluidine at a pH 10.0 - 10.5 at 15°C for 10 days)	20 ml/l
Surface-active agent (sulfopropylized addition product of 1 mol of nonylphenol with 13 mols of ethylene oxide)	5 ml/l
Acetaldehyde (20% solution)	10 ml/l
Temperature	20°C
Current density	3 A/dm <sup>2</sup>

### EXAMPLE 2

Divalent tin (used in the form of stannous cresolsulfonate)	27 g/l
Lead (used in the form of lead cresolsulfonate)	3 g/l
Free cresolsulfonic acid	80 g/l
Brightening agent (same as in Example 1)	25 ml/l
Surface active agent (sulfonized addition product of 1 mol of nonylphenol with 14 mols of ethylene oxide)	8 g/l
Acetaldehyde (20% solution)	10 ml/l
Temperature	25°C
Current density	5 A/dm <sup>2</sup>

### EXAMPLE 3

Divalent tin (used in form of stannous phenolsulfonate)	15 g/l
Lead (used in form of lead phenolsulfonate)	15 g/l
Free phenolsulfonic acid	150 g/l
Brightening agent (same as in Example 1)	25 ml/l
Surface active agent (addition product of 1 mol of isoctyl alcohol with 15 mols of ethylene oxide)	5 g/l
Acetaldehyde (20% solution)	5 ml/l
Temperature	25°C
Current density	8 A/dm <sup>2</sup>

### EXAMPLE 4

Divalent tin (used in the form of stannous phenolsulfonate)	20 g/l
Lead (used in the form of lead phenolsulfonate)	25 g/l
Free phenolsulfonic acid	80 g/l
Brightening agent (same as in Example 1)	40 ml/l

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Surface active agent	10 g/l
(addition product of 1 mol of nonylphenol with 14 mols of ethylene oxide)	
Acetaldehyde (20% solution)	5 ml/l
Temperature	30°C
Current density	10 A/dm <sup>2</sup>

## EXAMPLE 5

Divalent tin	15 g/l
(used in form of stannous phenolsulfonate)	
Lead	40 g/l
(used in form of lead phenolsulfonate)	
Free phenolsulfonic acid	100 g/l
Brightening agent	15 ml/l
(20% of solution of the precipitation which was extracted with isopropyl alcohol after the reaction of 4 mols of acetaldehyde with 1 mol of o-chloroaniline)	
Surface active agent (same as in Example 1)	15 g/l
Acetaldehyde (20% solution)	10 ml/l
Temperature	18°C
Current density	3 A/dm <sup>2</sup>

## EXAMPLE 6

Divalent tin	15 g/l
(used in the form of stannous phenolsulfate)	
Lead	10 g/l
(used in the form of lead phenolsulfonate)	
Free phenolsulfonic acid	100 g/l
Brightening agent	15 ml/l
(20% of solution of the precipitation which was extracted with isopropyl alcohol after the reaction of 3 mols of propion aldehyde with 1 mol of aniline)	
Surface active agent (same as in Example 1)	15 g/l
Acetaldehyde (20% solution)	10 ml/l
Temperature	18°C
Current density	3 A/dm <sup>2</sup>

Generally, both operative concentration range and preferred concentration range of the components of the both are as follows:

	(operative range)	(preferred range)
Total Metal (divalent tin and Lead)	10-60 g/l	15-50 g/l
Free cresolsulfonic acid or phenolsulfonic acid	50-200 g/l	75-150 g/l
Brightening agent	5-40 g/l (or 15-50 ml/l)	10-30 g/l
Surface active agent	2-30 g/l	3-15 g/l
Acetaldehyde (20% solution)	2-20 ml/l	3-15 ml/l

When the electroplating was carried out with moving the anode slowly under the condition of the solution compositions as shown in the above examples, bright deposition of tin-lead alloy was obtained in every case of the examples without lapsing or preliminary electrolysis. As the result of tests where the plating was carried out in various current densities, bright deposits were obtained respectively in the range of current density of 0.5-10 A/dm<sup>2</sup> in Example 1, 0.1-15 A/dm<sup>2</sup> in Example 2, 1-10 A/dm<sup>2</sup> in Example 3, and 3-20 A/dm<sup>2</sup> in Example 4. Also when phenolsulfonate and free phenolsulfonic acid in the above examples were substituted with cresolsulfonate and free cresolsulfonic acid, substantially the same result was obtained.

The acetaldehyde is conveniently added in the form of a 20% solution (in water). The use of acetaldehyde in place of formaldehyde has the advantage that the

bath is more stable and does not tend to form precipitates as do such baths containing formaldehyde.

The relative proportion of tin to the total dissolved tin plus lead in the electrolyte is preferably between about 40 and 99%.

In the above examples, the composition of deposits obtained when using a current density of more than 3 A/dm<sup>2</sup>, were nearly equal to the proportions of metals in the solutions. When using a current density of less than 3 A/dm<sup>2</sup>, it was observed that the proportion of lead in the deposit increased as the current density decreased. However, the rate of said increase was almost equal to that in case of non-bright deposition of the alloy which was obtained from a plating solution without the brightening agent. Therefore, when the concentration of metals in the plating solution and the current density utilized were known, it was able to predict exactly the composition of deposited alloy irrespective of whether it was bright or non-bright, and also the degree of brightness.

It is known that in the conventional industrial method of bright plating of tin-lead alloy where salts of borofluoric acid is used, the content of tin relative to lead in the deposit obtained at a current density of less than 10 A/dm<sup>2</sup> is much higher than in the plating solution. Furthermore, it is also known that the composition of the deposit is very variable with both the concentrations of various additives and the degree of brightness.

The surface active agent and acetaldehyde are used as components of our plating solution in order to enlarge the range of current density which could provide good, bright plating of alloy. There has been a general tendency that the range of current density to provide bright plating becomes higher as the amount of added acetaldehyde becomes less. Although the compositions of the solution and their conditions in the above-mentioned examples were illustrated for rack plating, this invention can be applied to continuous plating and barrel plating.

In this specification and claims, the 20% solution of acetaldehyde is percent by weight.

We claim:

1. An aqueous tin-lead alloy electroplating bath electrolyte consisting essentially of an acidic aqueous solution of (i) at least one sulphonate salt selected from the group consisting of the phenolsulfonate and cresolsulfonate salts of divalent tin and lead, the total of divalent tin and lead being between 10 and 60 g/l, and the total of free phenolsulfonic acid and free cresolsulfonic acid being between 50 and 200 g/l, (ii) between 15 and 50 ml/l of a 20% by weight solution of a brightening agent prepared by reacting an aliphatic aldehyde with an aromatic primary amine under alkaline conditions, and (iii) between 2 and 20 ml/l of acetaldehyde calculated as a 20% by weight aqueous solution, said divalent tin being between 40 and 99% of the total of divalent tin and lead in the electrolyte, said brightening agent being prepared by reacting 5 moles of acetaldehyde and one mole of toluidine for 10 days at a pH between 10.0 and 10.5 and at a temperature of 15°C, and then extracting the reaction product with isopropyl alcohol.

2. The electrolyte of claim 1 wherein (a) said total divalent tin and lead is present in an amount between 15 and 50 g/l, and (b) said total of phenolsulfonic and cresolsulfonic free acid is in an amount between 75 and 150 g/l, (c) said reaction product is present in an

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amount between 10 and 30 g/l, and (d) containing between 3 and 15 ml/l of said acetaldehyde solution.

3. The electrolyte of claim 2 wherein said aromatic primary amine is selected from the group consisting of o-toluidine, o-chloroaniline and aniline.

4. A method of electrodepositing bright tin-lead alloy comprising positioning an anode and a cathode in the electrolyte of claim 1 and passing a current from the anode to the cathode to electrodeposit tin-lead alloy on said cathode, the ratio of tin to lead in said tin-lead alloy electrodeposit corresponding to the ratio of tin to lead in said electrolyte.

5. A process for the bright electroplating of a substrate comprising the steps of:

positioning said substrate in an electroplating bath electrolyte containing tin and lead and electrodepositing tin and lead on said substrate from said

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electrolyte in a bright electrodeposit, said electrolyte consisting of at least one salt selected from the group consisting of the phenolsulfonate and cresolsulfonate salts of divalent tin and lead, the total of divalent tin and lead being substantially 10 to 60 g per liter, the divalent tin being between 40 and 99% of the total divalent tin and lead in the electrolyte, the total free phenolsulfonic acid or cresolsulfonic acid being between 50 and 200 g/liter, between 10 and 30 g/liter of a brightening agent prepared by reacting 5 moles of acid acetaldehyde for each mole of toluidine for 10 days at a pH between 10.0 and 10.5 at a temperature of 15 C and extracting the reaction product with isopropyl alcohol, and between 2 and 20 ml/liter of acetaldehyde calculated as a 20% by weight aqueous solution.

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