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1.

ELECTRODEPOSITION OF TIN AND TIN ALLOYS

The present invention relates to depositing tin as well as copper or rhodium alloys thereof on various substrates; more particularly the invention pertains to the deposition of bright, metallic tin from stable baths wherein the tin is in the form of divalent tin sulphate or fluoroborate, e.g. stannous sulphate or fluoroborate.

- There is a substantial body of prior art patents concerned with tin or tin alloy electroplating baths and processes for utilizing the same. Some of the more relevant patents for the present purposes include U.S. Patents 3,730,853 (Sedlacek et al.); 3,749,649 (Valayil); 3,769,182 (Beckwith et al.); 3,758,939 (Hsu); 3,850,765 (Karustis, Jr. et al.); 3,875,029 (Rosenberg et al.); 3,905,878 (Dohi et al.); 3,929,749 (Passal); 3,954,573 (Dahlgren et al.); 3,956,123 (Rosenberg et al.); 3,977,949 (Rosenberg); 4,000,047 (Ostrow et al.); 4,135,991 (Canaris et al.); 4,118,289 (Hsu); and British Patents 1,351,875 and 1,408,148.
- Despite the existence of this extensive literature and the various formulations which have been suggested for commercial applications, there is still a need for electroplating baths which will effectively deposit bright metallic tin on various substrates. Another important characteristic is bath stability, especially premature tin compound precipitation in the bath. The variety of bath formulations proposed heretofore reveal, moreover, that all of the ingredients employed in the bath formulation must be taken into consideration not only with respect to the type of deposit obtained but also with respect to questions such as bath stability

and by-product formation.

The present invention aims to provide a tin electroplating bath which ensures the deposition of bright metallic tin on various substrates.

5. The present invention also aims to provide a divalent tin electroplating bath of improved stability.

The present invention also aims to provide an improved electroplating bath for the deposition of alloys of tin with copper and/or rhodium.

10. We have now found that by utilizing certain aromatic sulphonic acid additives in conjunction with certain other additives an improved tin electroplating bath, formulated with bath soluble divalent tin compounds, can be achieved. The resulting bath not only leads to the deposition of bright metallic tin but is further characterized by outstanding stability.

15. The other bath ingredients will comprise an inorganic acid, an aromatic amine brightener, and a nonionic surface active agent. Preferably, the bath will also contain an aliphatic aldehyde brightener.

Copper or rhodium metals may also be effectively codeposited with tin from electroplating baths in accordance with the present invention.

20. The electroplating baths of the present invention are formulated with divalent tin in the form of a bath soluble compound. Typical of such compounds are stannous sulphate, stannous fluoroborate and stannous chloride.

25. Free inorganic acid is also present in amounts sufficient to provide conductivity, maintain the bath pH not in excess of about 2.0 and maintain the solubility of the metal salts. It will be understood that the particular acid
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used will correspond to the anion of the divalent tin compound, e.g. sulphuric acid when a sulphate is used, fluoroboric acid when a fluoroborate is used and hydrochloric acid when a chloride is used.

5. The brightener system preferably comprises one or more aromatic amines and, most preferably will comprise a combination of one or more aromatic amines and aliphatic aldehydes. The aromatic or aryl amines useful for use in the baths of the present invention
10. include o-toluidine; p-toluidine; m-toluidine; aniline and o-chloroaniline. For most purposes the use of o-chloroaniline is preferred.

Suitable aliphatic aldehydes are those containing from 1 to 4 carbon atoms and include, for example,

15. formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and crotonaldehyde. In this invention the preferred aldehyde is formaldehyde or formalin, which is a 37% aqueous solution of formaldehyde.

20. Nonionic surfactants are employed in the bath to provide grain refinement of the electrodeposit. These can be commercially available materials such as nonyl phenoxy polyethylene oxide ethanol e.g. Igelpal (Registered Trade Mark) CO630 and Triton (Registered Trade Mark) Q515; ethoxylated alkylolamide e.g. Amidex (Registered Trade Mark) L5 and C3; and alkyl phenyl polyglycoletherethylene oxide e.g. Newtronix (Registered Trade Mark) 675.
- 25.

30. Nonionic surface active agents which have been found to be particularly effective for the present purposes are the polyoxyalkylene ethers, where the alkylene group contains from 2 to 20 carbon atoms. Polyoxyethylene ethers having from 10 to 20 moles of ethylene

oxide per mole of lipophilic groups are preferred, and include such surfactants as polyoxyethylene lauryl ether (sold under the tradename Brij (Registered Trade Mark) 25-SP).

5. As previously described, the essential feature of the present invention is to utilize an aromatic sulphonic acid compound in conjunction with the bath ingredients set forth above. The sulphonic acid compounds maintain stability of the plating bath and provide
10. supplemental brightening and grain refinement to the electrodeposit. Preferred aromatic sulphonic acids are:
- o-cresol sulphonic acid
 - m-cresol sulphonic acid
 - phenol sulphonic acid
15. Other phenol sulphonic acid derivatives of phenol and cresol which could be employed include for examples:
- 2,6-dimethyl phenol sulphonic acid
 - 2-chloro, 6-methyl phenol sulphonic acid
20. 2,4-dimethyl phenol sulphonic acid
- 2,4,6-trimethyl phenol sulphonic acid
 - m-cresol sulphonic acid
 - p-cresol sulphonic acid

- Sulphonic acid derivatives of alpha- and beta-naphthols
25. are also possible candidates as the aromatic sulphonic acid ingredient. Additionally, the bath soluble salts of the above acids, such as the alkali metal salts, may be used instead of or in addition to the acid.

- In formulating the plating baths of the present
30. invention, the divalent tin compound will be used in an amount at least sufficient to deposit tin on the substrate

to be plated, up to its maximum solubility in the bath. The inorganic acid will be present in an amount sufficient to maintain the pH of the plating bath not in excess of about 2.0. The aromatic amine or the combination of the aromatic amine and the aliphatic aldehyde will be present in amounts at least sufficient to impart brightness to the tin electrodeposit, while the nonionic surfactant will be present in the bath in a grain refining amount. The aromatic sulphonic acid derivative will be present in an amount sufficient to maintain the stability of the plating bath and to enhance the brightness of the electrodeposit.

More specifically, the ingredients of the aqueous electroplating baths of this invention will be present in amounts within the following ranges:

15.	<u>Ingredients</u>	<u>Amounts</u>	<u>(grams/litre)</u>
		<u>Typical</u>	<u>Preferred</u>
	(1) Tin (II), as stannous sulphate, fluoroborate or chloride	5-50	15-30
20.	(2) Sulphuric, fluoroboric or hydrochloric acid	100-250	160-190
	(3) Aromatic Amine	0.3-15	0.5-1.5
	(4) Aliphatic Aldehyde	0.5-11	0.9-5.4
	(5) Nonionic surfactant	0.1-20	0.5-2.5
25..	(6) Aromatic sulphonic acid derivative	0.5-30	3-9

The pH of the bath will not be in excess of about 2.0 and will usually be less than about 1, with ranges from about 0 to 0.5 being typical and ranges from about 0 to 0.3 being preferred. Electroplating temperatures and current densities used will be those at which there

are no adverse effects on either the plating bath or the electrodeposit produced. Typically, the temperatures will be from about 10°C to 40°C, with temperatures of about 15 to 25°C being preferred. Typical current

5. densities will be about 10 to 400 Amps/square foot (ASF) (1 to 40 Amps/square decimetre (ASD)) and preferably about 25 to 200 ASF (2.5 to 20 ASD).

- The substrates which may be satisfactorily plated utilizing the electroplating baths of this invention
10. include most metallic substrates, except zinc, and include copper, copper alloys, iron, steel, nickel, and nickel alloys. Additionally, non-metallic substrates that have been treated to provide sufficient conductivity may also be plated using the bath and plating process according to
15. the present invention.

- Another aspect of this invention involves the discovery that copper and rhodium metals can be co-deposited with tin on the above mentioned substrates using the electroplating baths described above without the
20. need for additional additives or complexing agents. In contrast, metals such as nickel, iron and indium do not codeposit under the same conditions.

- Typically, the copper or rhodium is added to the bath as bath soluble compounds, preferably having the
25. same anions as the divalent tin compounds. The amounts of such compounds added are preferably sufficient to provide up to about 5% by weight of copper or rhodium, as codeposited alloying metal, alloyed with the tin, in the electrodeposit. Typical amounts of copper and rhodium
30. in the electroplating baths to provide such quantities

of the codeposited alloying metal in the elctrodeposit are about 0.2 to 4 grams/litre and 0.2 to 2 grams/litre, respectively.

- The invention may be put into practice in various
5. ways and certain sepcific embodiments will be described to illustrate the invention with reference to the accompanying examples.

Example I

10.

An electroplating bath was prepared from the ingredients set forth below:

	<u>Ingredients</u>	<u>Amount g/l</u>
15.	Tin (II), as stannous sulphate	22.5
	Sulphuric Acid	175
	o-chloroaniline	1.0, cc/l
	Formalin	10, cc/l
	Polyoxyethylene lauryl ether	1.0
20.	o-Cresol sulphonic acid	5.0
	Water	Remainder

- The resulting bath was stable and was operated at 20°C at a current density of 30 ASF (3 ASD) with rapid
25. agitation to plate a copper panel. The tin deposit thus formed had a very bright appearance.

Examples IIA to IIC

30. We have found that there is a side reaction between formaldehyde and the sulphonic acid which causes

(41)

a precipitate to form and settle out of the bath solution. However, we have further found that if the ortho position, and to a lesser extent the meta position, of the phenol sulphonic acid is blocked by methyl groups, as in o-cresol

5. sulphonic acid, this undesirable side reaction, and hence the precipitation, slows down. The other aspects of Example I such as work load, and degree of agitation, may also be further optimized to minimize, if not eliminate, this precipitate.

10. Example 1 was repeated to test the stability of the bath using a number of other sulphonic acids. The results were as follows:-

<u>Example</u>	<u>Additive</u>	<u>Amount (ml/l)</u>	<u>Stability (hrs)</u>
15. IIA	o-Cresol sulphonic acid (65%)	8	24
IIB	m-Cresol sulphonic acid (33%)	6	16
20. IIC	Phenol sulphonic acid (65%)	10	12

Example III

25. An electroplating bath was prepared for the following ingredients:

<u>Ingredients</u>	<u>Amount (g/l)</u>
Tin II, as stannous sulphate	30
30. Sulphuric acid	175
Copper, as copper sulphate	0.4
Formalin	10, cc/l

<u>Ingredients</u>	<u>Amount (g/l)</u>
o-Chloroaniline	0.4 cc/l
Polyoxyethylene lauryl ether	0.4
o-Cresol sulphonic acid	0.8

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The resulting bath was operated at 60 ASF (6 ASD) and produced a tin/copper alloy deposit containing 1.0% copper. The deposit was semi-bright.

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Examples IVA to IVD

Example III was repeated but the copper was replaced by rhodium at a concentration of 0.5 g/l of rhodium sulphate (Example IVA). The bath was operated at 60 ASF (6 ASD) and produced a very bright tin/rhodium alloy deposit containing 0.07% rhodium.

When nickel (Example IVB), iron (Example IVC), or indium (Example IVD) were employed in this bath they failed to codeposit with the metallic tin.

20.

Examples VA and VB

To demonstrate the stability enhancing effects of an aromatic sulphonic acid in the tin electroplating baths of this invention the following baths were prepared.

<u>Example VA</u>	<u>g/l</u>
Stannous sulphate	60
30. Sulphuric acid	180
o-Cresol sulphonic acid	5.6
Water	Remainder

10.

<u>Example VB</u>	<u>g/l</u>
Stannous sulphate	60
Sulphuric acid	180
Water	Remainder

5.

An electric air compressor with spargers was employed to pump air at a flow rate of approximately 15 cubic feet per minute (0.42 cubic metres/min.) through the baths in a 1 litre beaker.

10.

The concentration of stannic tin was measured in the baths at repeated intervals. The results are given in Table 1 below.

TABLE 1

15.

Stannic Tin Conc. (g/l)		
Example	VA	VB
Time period		
Start	0.3	0.5
5 days	2.2	9.1
10 days	3.5	13.6

20.

25.

In commercial operations air is normally present as a result of agitation, and becomes a serious problem because high rates of agitation will entrap substantial amounts of air which, in the absence of the aromatic sulphonic acid, will cause formation of stannic tin in the bath which is a measure of bath degradation.

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CLAIMS

1. An electroplating bath for the deposition of bright metallic tin or alloys of tin with copper and/or rhodium which comprises a bath soluble divalent tin compound in an amount sufficient to deposit tin on the substrate being
5. plated, an inorganic acid in an amount sufficient to maintain the bath pH not in excess of about 2.0, a brightening amount of an aromatic amine brightener, a nonionic surfactant, and an amount of an aromatic sulphonic acid sufficient to improve the stability of
10. the plating bath and enhance the brightness of the electrodeposit.
2. An aqueous electroplating bath for the deposition of bright, metallic tin on substrates which
15. comprises:
 - (a) Stannous sulphate or fluoroborate in an amount of 5 to 50 g/l,
 - (b) sulphuric or fluoroboric acid in an amount of 100 to 250 g/l,
 20. (c) an aromatic amine brightener in an amount of 0.3 to 15 g/l,
 - (d) an aliphatic aldehyde brightener in an amount of 0.5 to 11 g/l,
 - (e) a polyoxyalkylene ether in an amount of 0.1 to 20
 25. g/l, and
 - (f) cresol or phenol sulphonic acid in an amount of 0.5 to 30 g/l.
3. An electroplating bath as claimed in Claim
30. 1 or Claim 2 in which there is also present a brightening amount of an aliphatic aldehyde brightener.



4. An electroplating bath as claimed in Claim 3, in which the said aliphatic aldehyde brightener is formaldehyde.

5. 5. An electroplating bath as claimed in anyone of the preceding claims in which the nonionic surfactant is a polyoxyalkylene ether.

10. 6. An electroplating bath as claimed in claim 5 in which the polyoxyalkylene ether is polyoxyethylene lauryl ether.

15. 7. An electroplating bath as claimed in anyone of the preceding claims in which the said aromatic amine brightener is o-chloroaniline.

20. 8. An electroplating bath as claimed in anyone of the preceding claims in which the divalent tin is stannous sulphate.

9. An electroplating bath as claimed in anyone of the preceding claims in which the acid is sulphuric acid.

25. 10. An electroplating bath for the deposition of bright, metallic tin on substrates which comprises:
(a) stannous sulphate in an amount of 5 to 50 g/l,
(b) sulphuric acid in an amount of 100 to
30. 250 g/l,



- (c) o-chloroaniline in an amount of 0.3 to 15 g/l,
- (d) formalin in an amount of 0.5 to 11 g/l,
- (e) polyoxyethylene lauryl ether in an amount of 0.1 to 20 g/l, and
- (f) a cresol sulphonic acid in an amount of 0.5 to 30 g/l.
11. An electroplating bath as claimed in anyone
10. of the preceding claims in which the aromatic sulphonic acid comprises cresol or phenol sulphonic acids or mixtures thereof.
12. An electroplating bath as claimed in Claim
15. 11 in which the aromatic sulphonic acid is o-cresol sulphonic acid.
13. An electroplating bath as claimed in anyone
- of the preceding claims which also contains as an alloying
20. metal copper or rhodium or a mixture thereof.
14. An electroplating bath as claimed in Claim
- 13 in which the alloying metal is in the form of its sulphate salt.
- 25.
15. An electroplating bath as claimed in Claim 1 substantially as specifically described herein with reference to anyone of Examples I, IIA, IIB, III or IVA.
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16. A method for the deposition of bright



metallic tin or alloys of tin and copper and/or rhodium on a substrate which comprises electroplating the said substrate in the plating bath as claimed in anyone of claims 1 to 15 for a period of time sufficient to form the desired electrodeposit on the substrate.

17. A method as claimed in Claim 16 substantially as specifically described herein with reference to anyone of Examples I, IIA, IIB or IVA.

18. A substrate whenever provided with a bright electrodeposit by a method as claimed in Claim 16 or claim 17.

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