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Passal

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[54] **TIN-LEAD ALLOY PLATING**

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[21] Appl. No.: **541,432**

Related U.S. Application Data

[63] Continuation of Ser. No. 210,148, Dec. 20, 1971, abandoned.

[52] **U.S. Cl.** ..... **204/43 S;**

[51] **Int. Cl.**[2] **C25D 3/56;** C25D 3/60

[58] **Field of Search** ..... 204/54 R, 542, 43 S, 53

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Primary Examiner—G. L. Kaplan

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[57] **ABSTRACT**

This invention relates to the electrodeposition of tin-lead alloys; tin-lead alloy plating compositions, tin-lead alloy plating baths; and to processes for the electrodeposition of tin-lead alloys in the presence of at least one polyether surfactant and at least one aryl hydroxy (—OH) compound as cooperating additives.

28 Claims, No Drawings

TIN-LEAD ALLOY PLATING

This is a continuation of application Ser. No. 210,148, filed Dec. 20, 1971, now abandoned.

BRIEF DESCRIPTION

This invention relates to the electrodeposition of an alloy of tin and lead; plating compositions, plating baths for the electrodeposition of an alloy of tin and lead, and to processes for the electrodeposition of an alloy of tin and lead in the presence of specific polyether additives. More specifically this invention provides as a novel additive for electrodepositing an alloy of tin and lead from baths containing a water soluble stannous salt and a water soluble lead salt, at least one polyether surfactant to yield a continuous, microcrystalline, uniform deposit having excellent low current density coverage.

There is increasing interest in the application of tin-lead alloy for brighter deposits for printed circuitry, the high speed deposition on strip and wire, and the soldering of contacts in electronic equipment and printed circuitry. The additives presently used in fluoborate baths are usually glue, gelatin, or high proteose peptones. These brighteners of the prior art are complex mixtures of materials, are generally of ill-defined and variable composition, and in use, due to accumulation of degradation products and strong tendency toward molding, may exhibit offensive odors.

The most common additive used for tin-lead alloy plating is a peptone. When a peptone is used as an additive it changes the deposit from a discontinuous, spongy, dendritic coating to a continuous, fairly fine-grained deposit which generally has a rather dark color and exhibits poor low current density coverage and throwing power. In use the peptone tends to hydrolyze and mold and may develop a very objectionable odor in the plating bath.

The results obtained by the practice of this invention are far superior to those attainable with the additive systems of the prior art.

The practice of this invention results in the following specific improvements:

1. The deposits are much lighter in color and approach a white color.
2. The deposits are very uniform and show substantially decreased grain size.
3. The deposits very definitely are more glossy although not highly reflective.
4. The low current density coverage is excellent and indicates possibly increased throwing power.

The deposits attained by practice of this invention have applications in the electronics and other fields to provide improved appearance of plated articles, improved solderability characteristics and improved resistance to staining in use.

It is an object of this invention to provide a new tin-lead alloy plating additive system which would utilize a compound which may be a single chemical entity and which would result in substantial improvement in process performance over those systems of the prior art.

It is also an object of this invention to provide improved baths for obtaining tin-lead alloy deposits having enhanced color and grain characteristics.

DETAILED DESCRIPTION

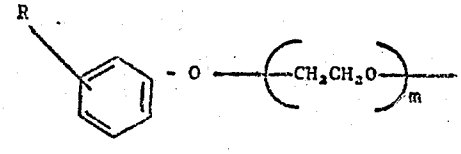
This invention is an aqueous bath for electrodepositing white, continuous, fine-grained tin-lead alloys comprising:

(a) 4 grams per liter to 53 grams per liter of stannous tin;
(b) 1 gram per liter to 85 grams per liter of lead;
(c) 100 grams per liter to 200 grams per liter free fluoboric acid;
(d) 4 grams per liter to 10 grams per liter of a polyether surfactant.
(e) 0.5 grams per liter to 1.0 gram per liter of an aryl hydroxy (-OH) compound selected from the group consisting of naphthols and substituted phenols.

According to another of its aspects this invention relates to a process of producing white, continuous, fine-grained tin-lead alloy electrodeposits which comprises passing current from an anode to a metal cathode through an aqueous bath composition containing at least one water soluble stannous salt, at least one water soluble lead salt, fluoboric acid, boric acid, at least one polyether surfactant, and at least one aryl hydroxy (—OH) compound.

The compositions and methods herein are applicable to barrel, rack and wire electroplating processes. The concentrations of tin and lead may be varied generally within the limits conventional in the art. For example, baths with a stannous tin content of 4 to 53 grams per liter and a lead content of 1 to 85 grams per liter may be utilized with the additives of the invention herein.

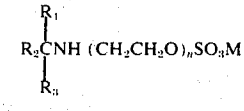
Polyether surfactants operable in the practice of this invention include aromatic polyethers and aliphatic polyethers. Preferably the wetting agent is a polyalkoxylated alkyl phenol. Typical polyalkoxylated alkyl phenols include polyethoxylated alkyl phenols having the formula:



wherein R represents and alkyl group of from 5 to 15 carbon atoms (preferably 9 carbon atoms) and m is an integer of at least 5 and preferably no more than 20.

Polyether surfactants are employed in amounts of about 4 grams per liter to 12 grams per liter (preferably about 8 grams per liter).

Other polyether surfactants which may be employed in amounts of 4 grams per liter to 12 grams per liter (preferably about 8 grams per liter) include nitrogen-containing aliphatic polyethers characterized by the following general formula:



wherein R_1, R_2 and R_3 represent a straight chain or branched alkyl group exhibiting 3 to 15 carbon atoms, n is an integer of at least 5 and no more than 10, and M

is a cation selected from the group consisting of hydrogen, sodium, potassium, and ammonium.

According to another of its embodiments, this invention relates to an electroplating bath for the electrodeposition of an alloy of tin and lead containing a water soluble stannous salt, a water soluble lead salt and containing as cooperating additives

1. a polyether surfactant containing at least 5 and no more than 20 ether oxygen atoms per molecule, and
2. an aryl hydroxy (—OH) compound

to give a continuous, microcrystalline, uniform deposit having excellent low current density coverage.

The aryl alcohols operable in the practice of this invention are naphthols and substituted phenols. The aryl hydroxy (—OH) compound should be present in an amount of 0.5 to 1 gram per liter.

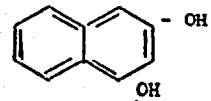
The naphthol compounds contain one or more hydroxy (—OH) groups. The naphthol compounds may contain inert substituents such as chloro, but should not contain negatively charged substituents.

The phenol compounds exhibit one or more hydroxy (—OH) groups. The phenol compounds may contain one or more but fewer than four inert substituents per benzene ring and may contain inert connecting groups such as sulfone ($-SO_2-$), but should not contain any negatively charged groups.

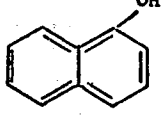
The cooperating additives are at least one polyether surfactant and at least one aryl hydroxide. The surfactant serves to transform the loosely adherent, spotty, sometimes dendritically crystalline tin-lead alloy deposit from an additive-free bath into a dense, continuous, adherent, microcrystalline deposit. The aryl hydroxide functions to greatly improve low current density coverage and throwing power.

Typical examples of naphthols and phenols which have been found to be effective are the following:

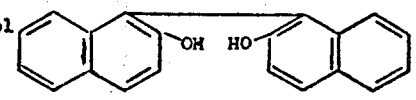
β-naphthol



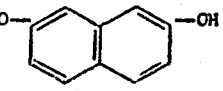
α-naphthol



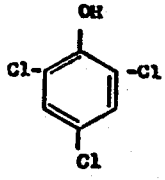
1,1'-Bi-2-naphthol



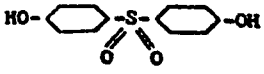
2,7-Naphthalenediol



2,4,6-Trichlorophenol



P,P'Dihydroxydiphenylsulfone



Stannous tin in solution supplies the tin contained in the deposited tin-lead alloy. In a freshly made bath containing 10 g/l tin and 90 g/l lead, approximately 85% of the tin will be in the stannous state, the remainder being stannic tin. Such a bath will give a deposit containing 10% tin. If the stannic tin increases and the stannous tin decreases, the percentage tin in the deposit will fall below 10%. However, at higher concentrations, for example 50 g/l tin and 35 g/l lead, there is less tendency for stannic tin to form in the bath.

In the normal operation of the bath, the stannous tin content remains fairly constant, resulting in a deposit of uniform tin content. However, if the solution is to be out of operation for some time, it is advisable to filter the bath and to protect it from the air as much as possible to minimize the formation of stannic tin.

Lead dissolved as fluoborate supplies the lead contained in the deposited tin-lead alloy.

Free fluoboric acid is maintained in the bath to provide the requisite acidity, to raise the conductivity, to give a fine-grained deposit, and to help prevent treeing. Its range may be from 100 to 200 g/l.

Boric acid is added to the bath to maintain stability of the bath. Approximately 25 g/l of boric acid have been found desirable but its concentration is not critical.

The preferred operating conditions, such as pH, temperature, and current density may vary depending upon

the particular bath composition and the nature of the article receiving the layer of tin-lead alloy electrodeposit. In general, good, tin-lead alloy electrodeposits may be obtained within a specific range of operating conditions.

The tin-lead alloy electroplating processes using the compositions of the invention may be carried out at temperatures of about 10°C. – 60°C. (preferably 15°C. – 20°C.) either with or without agitation. The temperature of the plating solution is usually the ambient temperature, say 35°C. or below, with lower temperatures giving optimum results, such as 15°C. – 20°C. In some operations, where substantial cell currents are used, resulting in a temperature elevation tendency, suitable cooling must be provided such as by circulating cool water through immersed cooling coils, by means of refrigeration machines, etc. Using an average current densities of 0.5 – 5.0 amperes per square decimeter (ASD), tin-lead alloy electrodeposits having average thicknesses of 0.25 – 25 microns may be obtained using plating times which may average 0.1 – 10 minutes.

If necessary, vigorous ad uniform agitation of the plating bath composition may be provided either by mechanical movement of the article being plated or by solution agitation during the electrodeposition. Such agitation may permit the use of high plating current densities on the article being plated.

In the plating of tin-lead alloy the parts may be plated on racks, i.e. on fixtures holding single or multiple parts which may all be the same or which may be different in size, geometrical configuration, etc. Parts may also be plated in bulk in rotating barrels and in this type of plating, usually used for plating of smaller parts which lend themselves to tumbling action, the barrel loads usually consist of the same part although mixed loads are sometimes plated. Because of the number, size, and shape complexity of parts it is important that the plating bath be so formulated as to provide the widest possible semi-glossy plate current density range. It is also important that the limiting current density, i.e. the current density at which the deposit ceases to be sound in structure and appearances, be as high as possible to allow for the wide variations in cathode current density which may be encountered due to the size and shape complexity of parts.

The polyether surfactant such as Tergitol Non-Ionic NP-35 may be added as a concentrated aqueous stock solution, say 100 grams per liter, in which form it would be added at a concentration, say, of 40 to 80 ml/l or 4 to 8% by volume.

The following examples are submitted for the purpose of illustration only, so that those skilled in the art of tin-lead plating may better understand the operation of the invention. These examples are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

A 60–40% lead alloy plating bath was prepared having the following composition:

stannous fluoborate concentrate (49.6% by wt.)	16.2% by vol.
lead fluoborate concentrate (50% by wt.)	6.3% by vol.
fluoboric acid (49% by wt.)	15.0% by vol.
boric acid	15.6 g/l
water	62.6% by vol.
to give	
stannous tin	52 g/l
lead	30 g/l
free fluoboric acid	100 g/l
free boric acid	25 g/l

The Hull Cell plating conditions were as follows:

solution volume	267 ml.
temperature	20°C.
agitation	magnetic stirring
cell current	1 ampere
time	5 minutes
anode	slab of 60% tin - 40% lead alloy
cathode	polished brass

To the above bath was added 8 grams per liter of a nonylphenolethylene oxide condensate containing about fifteen ethylene oxide groups per molecule (sold as Tergitol Non-Ionic NP-35 by Union Carbide Chemical Corporation).

The deposits from this system were white, continuous, and fine-grained.

EXAMPLE 2

Addition of β-Napthol Additive

A stock solution of β-Napthol was prepared by adding 144.2 grams (1 mole) of powdered U.S.P. grade of β-Naphthol to water while stirring magnetically. 50 grams of C.P. NaOH pellets previously dissolved in 200 ml. water was added; stirring was continued until the β-Naphthol dissolved. 3 grams of activated carbon (Darco S 51-Red Label or equivalent) were added and stirring was continued for 1 hour and then filtration was performed. The filtrate was diluted with water to 1440 ml. to give a 100 g/l solution of β-Naphthol. 1 part by volume of purified 100 g/l β-Naphthol stock solution was mixed with 1 part by volume of a 100 g/l stock solution of Tergitol Non-Ionic NP-35.

10 ml/l of the stock solution was added to the bath composition of Example 1 to give 0.5 g.l of β-Naphthol. The β-Naphthol was completely dissolved and the resulting deposit was white, semi-glossy, microcrystalline, continuous, and fine-grained, with no defects and much better low current density coverage than that attained in Example 1.

EXAMPLE 3 (Comparison)

A system identical with that of Example 1, except that the polyether surfactant was omitted, resulted in a dendritic, loosely adherent, spongy, discontinuous deposit with very poor low current density coverage on both the front and the back of the cathode.

The three foregoing examples conclusively show that in fluoborate tin-lead plating the combination of a non-ionic polyether surfactant such as Tergitol Non-Inoic NP-35 with β-Naphthol has been found to give finer-grained, glossier, whiter deposits with greatly increased low current density coverage, which is potentially very useful in printed circuitry for through-hole plating.

Thus, if there is added to the fluoborate tin-lead plating bath the euivalent of 4 to 8 g/l, say, of Tergitol Non-Ionic NP-35 there is obtained a fine-grained, semi-glossy, white, continuous deposit instead of the dendritic, spongy, discontinuous deposit obtained from the additive-free bath in the Hull Cell. If the naphthol or phenol compound is then added in a concentration, say, of 0.5 to 1 g/l, all the good deposit characteristics are retained but, in addition, excellent low current

density coverage is obtained. If to the fluoborate tin-lead plating bath there is added only 0.5 to 1 g/l of the naphthol or phenol and no polyether surfactant (the naphthol or phenol may be added in the form of a solution in a solvent such as Cellosolve or as an aqueous solution of the sodium salt whereupon most of the naphthol or phenol may precipitate out giving a quite low, say less than 0.1 g/l, concentration at saturation) the deposit may be white, continuous, fine-grained with good low current density coverage but in the high current density end of the range the deposit most likely will be dendritic or spongy and in other portions of the range defects such as pits, striations, etc. may occur wherever the precipitate adheres. To illustrate:

EXAMPLE 4 (Comparison)

Aryl Alcohol Additive Alone

A system identical with that of Example 2, except that the polyether surfactant was omitted, resulted in a defective deposit that was dendritic in high current density areas.

EXAMPLE 5 (Comparison)

A fluoborate tin plating bath was prepared having the following composition:

stannous fluoborate concentrate (49.6%)	25.2% by vol.
fluoboric acid (49%)	14.2% by vol.
water	60.6% by vol.

(to give 81 g/l tin and 100 g/l of free fluoboric acid).

This system resulted in a porous, discontinuous deposit with very poor low current density coverage.

EXAMPLE 6 (Comparison)

To a fluoborate tin bath identical with that of Example 5 was added 8 g/l of a nonylphenol-ethylene oxide condensate containing about fifteen ethylene oxide groups per molecule. The resulting deposit tended to be macrocrystalline with very poor low current density coverage.

EXAMPLE 7 (Comparision)

When 10 ml/l of a stock solution of β-Naphthol (prepared as in Example 2) was added to the bath of Example 6 a white, fairly fine-grained, continuous deposit resulted, but the low current density coverage was poor.

EXAMPLE 8

To the bath of Example 7 was added 4 ml/l of lead fluoborate concentrate; the resulting deposit was white, fine-grained, and continous with excellent low current density coverage.

Thus, in a fluoborate tin plating bath the addition of, say 4 to 8 g/l of polyether surfactant plus 0.5 to 1 g/l, say, of β-Naphthol, a white, macrocrystalline, matte deposit which is continuous will be obtained in the Hull Cell instead of the coarsely crystalline, discontinuous, porous (only scattered islands of tin crystal deposit) deposit from the aditive-free bath; the low current density coverage however will be poor. On the addition of a low concentration of lead fluoborate to give a deposit containing 2 to 5 % by weight of lead, a white, microcrystalline, uniform, continous deposit is now obtained with excellent low current density coverage i.e. the addition of lead has a remarkable effect on increasing low current density coverage.

Similar results will be obtained with other phenol and naphthol compounds. Preparation of two other typical stock solutions are as follows.

EXAMPLE 9

Preparation of Solution of 2,4,6-Trichlorophenol

Dissolved were 2,4,6-trichlorophenol (100 grams) and NaOH (25 grams) in about 900 ml. water. The solution was treated with 3 grams of activated carbon for 2 hours and was the filtered and the filtrate diluted to 1 liter with water. To prepare the additive stock solution, 1 part by volume of the solution was mixed with 1 part by volume of a 100 g/l stock solution of Tergitol Non-Ionic NP-35.

EXAMPLE 10

Preparation of Solution of 4,4'-Dihydroxydiphenylsulfone

Dissolved were 100 grams of 4,4'-dihydroxydiphenysulfone and 40 grams NaOH in about 900 ml. water. The solution was treated with 3 grams of activated carbon for 3 hours, filtered and the filtrate diluted to 1 liter with water. To prepare the additive stock solution, 1 part by volume of the resulting solution is mixed with 1 part by volume of a 100 g/l stock solution of Tergitol Non-Inonic NP-35.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process of producing white, continuous, fine-grained tin-lead alloy electrodeposits exhibiting excellent low density characteristics which comprises passing current from an anode to a metal cathode through an aqueous acidic bath composition consisting essentially of at least one water soluble stannous tin salt, at least one water soluble lead salt providing about 1.0 gram per liter to 85.0 grams per liter of lead and cooperating additives consistinig of 4 grams per liter to 12 grams per liter of at least one polyether surfactant and 0.5 gram per liter to 1.0 gram per liter of at least one aryl hydroxy (—OH) compound selected from the grooup consisting of naphthols and substituted phenols in the absence of other brightening agents.

2. The process of claim **1** wherein said aryl hydroxy (—OH) compound is selected from the group consisting of naphthols and substituted phenols.

3. The process of claim **2** wherein said aryl hydroxy (—OH) compound is β-naphthol.

4. The process of claim **2** wherein said aryl hydroxy (—OH) compound is 2,4,6 trichlorophenol.

5. The process of claim **2** wherein said aryl hydroxy (—OH) compound is p,p' dihydroxdiphenylsulfone.

6. The process of claim **2** wherein said aryl hydroxy (—OH) compound is 2,7-naphthalenediol.

7. The process of claim **2** wherein said aryl hydroxy (—OH) compound is 1,1'-**bi**-2-naphthol.

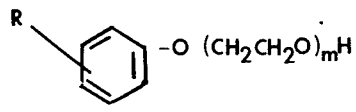
8. The process of claim **2** wherein said aryl hydroxy (—OH) compound is α-naphthol.

9. The process of claim **1** wherein said tin-lead alloy is substantially 60% tin and 40% lead.

10. The process of claim **6** wherein said polyether surfactant is a nonylphenol-ethylene oxide condensate

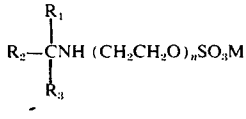
exhibiting about fifteen ethylene oxide groups per molecule.

11. The process of claim 1 wherein said polyether surfactant is of the formula:



wherein R is an alkyl group of 5–15 carbon atoms and is an integer 5–20.

12. The process of claim **1** wherein the water soluble alkoxylated wetting agent is of the formula:



wherein R_1, R_2 and R_3 are each straight chain or branched alkyl groups each exhibiting 3 to 10 carbon atoms, *n* is 5–10, and M is a cation selected from the group consisting of hydrogen, sodium, potassium, and ammonium.

13. The process of claim **1** wherein the water soluble stannous tin salt is stannous fluoborate and the water soluble lead salt is lead fluoborate.

14. A process for electrodepositing white, continuous, fine-grained tin-lead alloy electrodeposits which comprises passing current from an anode to a cathode through an aqueous acidic bath composition consisting essentially of:

a. 4 grams per liter to 53 grams per liter of stannous tin;
b. 1 gram per liter to 85 grams per liter of lead;
c. 100 grams per liter to 200 grams per liter of free fluoboric acid;
d. 4 grams per liter to 10 grams per liter of a polyether surfactant; and
e. 0.5 grams per liter to 1.0 gram per liter of an aryl hydroxy (—OH) compound selected from the group consisting of naphthols and substituted phenols.

15. A composition for providing white, continuous, fine-grained tin-lead alloy electrodeposits which comprises an aqueous acidic bath composition consisting of at least one water soluble stannous tin salt, at least one water soluble lead salt providing about 1.0 gram per liter to 85.0 grams per liter of lead and containing as cooperating additives 4 grams per liter to 12 grams per liter of at least one polyether surfactant and 0.5 gram per liter to 1.0 gram per liter of at least one aryl hydroxy (—OH) compound selected from the group consisting of naphthols and substituted phenols, in the absence of other brightening agents.

16. The composition of claim **15** wherein said aryl hydroxy (—OH) compound is selected from the group consisting of naphthols and substituted phenols.

17. The composition of claim **16** wherein said aryl hydroxy (—OH) compound is β-naphthol.

18. A composition as claimed in claim **16** wherein said aryl hydroxy (—OH) compound **13** 2,4,6 trichlorophenol.

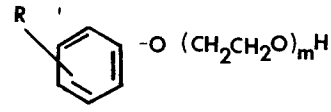
19. The composition of claim **16** wherein said aryl hydroxy (—OH) compound is p,p′ dihydroxydiphenylsulfone.

20. The composition of claim **16** wherein said aryl hydroxy (—OH) compound is 2,7-naphthalenediol.

21. The composition of claim **16** wherein said aryl hydroxy (—OH) compound is 1,1′-**bi**-2-naphthol.

22. The composition of claim **16** wherein said aryl hydroxy (—OH) compound is α-naphthol.

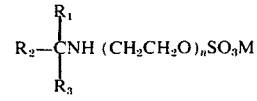
23. A composition as claimed in claim **15** wherein the polyether surfactant is of the formula:



wherein R is an alkyl group of 5–15 carbn atoms and *m* is an integer 5–20.

24. The composition of claim **23** wherein the said polyether surfactant is a nonylphenol-ethylene oxide condensate exhibiting about fifteen ethylene oxide groups per molecule.

25. A composition as claimed in claim **15** wherein the polyether surfactant is of the formula:



wherein R_1, R_2 and R_3 are each straight chain or branched alkyl groups each exhibiting 3 to 10 carbon atoms, *n* is 5 to 10, and M is a cation selected from the group consisting of hydrogen, sodium, potassium and ammonium.

26. The composition of claim **15** wherein said water soluble stannous tin salt is stannous fluoborate and said water soluble lead salt is lead fluoborate.

27. The composition of claim **15** wherein the said tin-lead alloy is substantially 60% tin and 40% lead.

28. A composition for providing white, continuous, fine-grained tin-lead alloy electrodeposits consisting of an aqueous acidic bath composition consisting of:

a. 4 grams per liter to 53 grams per liter of stannous tin;
b. 1 gram per liter to 85 grams per liter of lead;
c. 100 grams per liter to 200 grams per liter of free fluoboric acid;
d. 4 grams per liter to 10 grams per liter of a polyether surfactant; and
e. 0.5 grams per liter to 1.0 gram per liter of an aryl hydroxy (—OH) compound selected from the group consisting of naphthols and substituted phenols.

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