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BRIGHT TIN-LEAD ALLOY PLATING

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U.S. Cl. 204—43 S 44 Claims

ABSTRACT OF THE DISCLOSURE

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:

(a) at least one polyether surfactant; and
(b) at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

A preferred aspect of this invention lies in the electrodeposition of tin-lead alloys in the presence of a combination of:

(a) at least one polyether surfactant;
(b) at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent;
(c) at least one aliphatic amine or at least one compound producing an aliphatic amine; and
(d) at least one anti-oxidant or oxygen acceptor.

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 a specific combination of additives. More specifically this invention provides as a novel combination of additives for electrodepositing an alloy having about 60% tin and about 40% lead from baths containing a water soluble stannous salt and a water soluble lead salt, at least one polyether surfactant, and at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

Background

A tin-lead alloy containing about 60% tin and about 40% lead by weight, commonly known as "solder-plate," obtained by electrodeposition from a stannous fluoborate-lead fluoborate system, has had extensive application for many years. Some of its applications have been the following:

(A) As an easily soldered deposit for making electrical connections.
(B) As an easily soldered deposit for printed circuitry which is applied on the electrically conductive pattern and which resists attack by various etching solutions used to remove copper from areas where it is not needed in order to leave a conductive pattern.

The alloy has been generally plated from a fluoborate system utilizing certain additives, usually of organic nature such as peptones and animal glue, to give continuity of deposit, to refine the crystalline structure, and to eliminate the tendency toward loosely adherent, dendritic deposit growth. At best, however, the prior art deposits have been generally dull with a dark cast. The low current density coverage and throwing power also have been generally poor which may be a serious disadvantage particularly in printed circuitry through-hole plating. Another disadvantage of prior art deposits has been tendency toward staining, finger-marking on handling, and decreased solderability on storage.

It has become a desideratum in the art of solder-plating, particularly under high production conditions for both rack and barrel plating applications where freedom from staining and decreased solderability are particularly important, to attain a ductile, highly lustrous, uniformly fine-grained deposit throughout a wide cathode current density range.

It has also become a desideratum to obtain highly lustrous deposits which have enhanced resistance to staining and finger-marking, and which will maintain their appearance and solderability over relatively long time periods of storage.

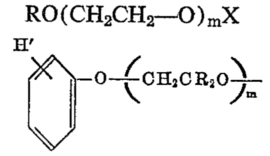
Detailed description

This invention relates to a process of producing lustrous, continuous, ductile, 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 aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

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 this art. For example, baths with a stannous tin ion content of 5 to 55 g./l. and a lead ion content of 20 to 30 g./l. may be utilized with the additives of the invention herein.

Type A polyether surfactants operable in the practice of this invention are polyether surfactants which may 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 formulae:

$$RO(CH_2CH_2-O)_mX \qquad (I)$$



(II)

wherein R represents an alkyl group of from 4 to 18 carbon atoms, R′ is an aliphatic radical containing 8 to 20 carbon atoms, *m* is an integer of at least 4 and no more than 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is selected from the group consisting of sodium, potassium, ammonium, magnesium, lead, tin, calcium, rubidium, cesium, or any other bath-compatible cation.

Operable polyether surfactants include nitrogen-containing aliphatic polyethers characterized by the following general formulae:

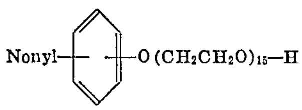
$$R_2\overset{R_1}{\underset{R_3}{C}}NH(CH_2CH_2O)_nX \qquad (III)$$

$$R'_4-\underset{\underset{O}{\|}}{C}NH(CH_2CH_2O)_n-X \qquad (IV)$$

wherein R_1, R_2, R_3 and R_4 represent a straight or branched chain alkyl group exhibiting 8 to 18 carbon atoms, *n* is an integer of at least 4 and no more than 100, and X is selected from the group consisting of hydrogen, SO_3M, PO_4M_2 where M is selected from the group consisting of sodium, potassium, ammonium, magnesium, lead, tin, calcium, rubidium, cesium, or any other bath-compatible cation.

Polyether surfactants are employed singly in amounts of about 1 g./l. to 10 g./l., and in combination from 10 g./l. to 20 g./l.

Typical specific compounds are the following with their concentration ranges varying singly from 1 g./l. to 10 g./l. and in combination from 10 g./l. to 20 g./l.:



(sold as Tergitol Non-Ionic NP-35)

$R_2-C(R_1)(R_3)-NH(C_2H_4O)_nSO_3Na$ $R_1+R_2+R_3$=12-14 C atoms and n=15

(sold as Triton QS-15)

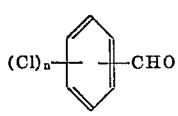
$R_2-C(R_1)(R_3)-NH(C_2H_4O)_nH$ $R_1+R_2+R_3$=12-14 C atoms and n=15

(sold as Priminox R-15)

The polyether surfactants may be used in the form of aqueous stock solutions.

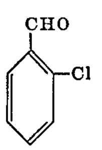
Thus the polyether surfactant such as Tergitol Non-Ionic NP-35 may be added as a concentrated aqueous stock solution, say 100 g./l., in which form it would be added at a concentration of 40 ml./l. or 4% by volume.

Type B chlorinated aromatic aldehydes operable in the practice of this invention are aromatic aldehydes having at least one chloro substituent of the formula:

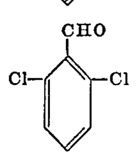


where n is 1 or 2

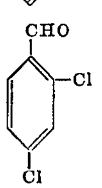
Typical specific compounds are the following with their concentration ranges varying from 0.1 g./l. to 1 g./l. and used singly or in combination:



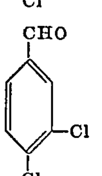
o-Chlorobenzaldehyde (a preferred compound because of its cost being relatively low and its easy availability)



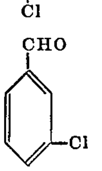
2,6-dichlorobenzaldehyde



2,4-dichlorobenzaldehyde



3,4-dichlorobenzaldehyde



m-Chlorobenzaldehyde

Compounds which are effective due to the release of a chlorinated aromatic aldehyde on being added to the plating bath are the following structural configurations:

(1) $R-CH(OH)-SO_3Na$ (aldehyde-bisulfite adducts)

(2) $R-CH=N-R'$ (R'=aliphatic or aromatic group)

(3) $R-CH=N-NHR''$ (R''=aromatic group such as phenyl)

(4) $R-CH=N-NHC(=O)-NH_2$ (semi-carbazones)

(5) $R-CH=N-OH$ (oximes)

(6) $R-CH=(OR''')_2$ (R'''=alkyl group—acetals)

In the above compounds, R is an aromatic moiety such as phenyl containing 1 or 2 chloro groups directly bonded to the aromatic ring.

Compounds of Type B may be used in the form of stock solutions in appropriate organic solvents (methanol, ethanol, isopropanol, acetone, etc.) or in mixtures of organic solvents (such as methanol plus water plus compounds of Type A, the latter imparting appreciable solubilizing action).

Although the cooperative use of compounds of Types A and B may give excellent results, particularly under barrel plating conditions, it has also been found that the addition of an aliphatic amine as a further cooperating additive will result in even more uniformly lustrous, pit-free and striation-free deposits.

Thus, 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:

(a) At least one polyether surfactant;

(b) At least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent; and

(c) At least one aliphatic amine or a compound producing an aliphatic amine.

Type C compounds which are aliphatic amines or compounds which liberate aliphatic amines on addition to the electroplating bath are of the formulae:

$$R-NH_2 \quad (V)$$

$$R-N=C(R')(R'') \quad (VI)$$

where R′, R″=hydrogen, alkyl or aromatic groups, and R=alkyl group, straight or branched chain with 3 to 20 C atoms.

Specific and preferred compounds are exemplified by:

$CH_3(CH_2)_{11}NH_2$ laurylamine
$CH_3(CH_2)_7NH_2$ octylamine

The aliphatic amine or aliphatic amine producing compounds are used in concentrations ranging from 0.25 g./l. to 5 g./l. depending on their degree of bath solubility. They may be used in the form of aqueous or organic solvent stock solutions or in mixtures of water and organic solvents.

A plating bath of the fluoborate type which may be used in the practice of this invention may consist of the following basic ingredients:

stannous fluoborate [$Sn(BF_4)_2$]
lead fluoborate [$Pb(BF_4)_2$]
fluoboric acid [HBF_4]
boric acid [H_3BO_3]

The stannous fluoborate is usually added as an aqueous concentrate containing typically 49.6% by weight of $Sn(BF_4)_2$ having a specific gravity of 1.60. The lead fluoborate is usually added as an aqueous concentrate containing typically 50% by weight of $Pb(BF_4)_2$ having a specific gravity of 1.75. The fluoboric acid is generally added as an aqueous concentrate typically 49% by weight of HBF_4 having a specific gravity of 1.37. The boric acid is usually added as a relatively pure grade of powdered or crystalline H_3BO_3. The fluoboric acid added in addition to the BF_4 anion associated with stannous tin and lead is usually referred to as "free fluoboric acid."

A typical concentration of bath constituents and a preferred bath made-up concentration are as follows, in grams per liter (g.l.):

	Range, g./l.	Preferred, g./l.
$Sn(BF_4)_2$	110–135	135
$Pb(BF_4)_2$	37–55	46
HBF_4	100–200	120
H_3BO_3	10–40	30
Equivalent to—		
Sn^{+2}	45–55	55
Pb^{+2}	20–30	25
Free fluoboric acid	100–200	120
Boric acid	10–40	30

Anodes generally consist of a cast or extruded tin-lead alloy containing 60% tin and 40% lead. In order to more consistently obtain an alloy composition at the cathode close to 60–40, the following operating conditions are generally used:

Temperature: 10° C.–60° C.
Cathode current density: 3.0 a.s.d. (amperes per square dm.)
Anode current density: 1.5 a.s.d.
Agitation: mild mechanical (150 to 700 cm. per minute) or slowly rotating barrel (2–5 r.p.m.)

Increasing the cathode current density over 3.0 a.s.d. will tend to increase the tin content of the deposit while decreasing the cathode current density below 3.0 a.s.d. will tend to decrease the tin content of the deposit. Although ideally a 60–40% alloy is desired, in actual commercial operation a tin content of 60±10% by weight and a lead content of 40±10% by weight are generally acceptable and this means that some variation in tin and lead concentrations and in cathode current density may be tolerated.

This invention also lies in the adddition of an anti-oxidant or oxygen acceptor for substantially decreased tendency toward formation of precipitates of stannic basic salts. Operable anti-oxidants or oxygen acceptors include hydroquinone or substituted hydroquinone, pyrocatechol, pyrogallol, catechol, and aromatic sulfinates such as sodium benzene monosulfinate.

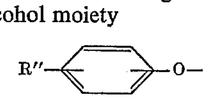
These compounds may be used singly or in combination in concentrations of about 0.5 g./l. to 5 g./l. depending on their bath solubility. They may be used in the form of aqueous or organic solvent stock solutions or they may be added directly to the plating bath with stirring to facilitate solution.

According to another of its embodiments, this invention is an aqueous solution for electrodepositing a bright, sound, smooth ductile alloy of tin and lead having about 60% tin and 40% lead comprising: 110 g./l. to 135 g./l. of stannous fluoborate; 37 g./l. to 55 g./l. of lead fluoborate; 100 g./l. to 200 g./l. of fluoboric acid; 10 g./l. to 40 g./l. of boric acid; and as a novel additive system:

(a) At least 1 g./l. of at least one polyether surfactant of the formulae:

$$R—(CH_2CH_2—O)_n—X$$

where R is an aliphatic alcohol moiety R'—O— where R' is an aliphatic radical containing 4 to 18 carbon atoms or an aromatic alcohol moiety



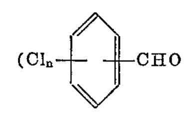
where R'' is an aliphatic radical containing 8 to 20 carbon atoms;

$$R'NH(CH_2CH_2O)_n—X$$

$$R'—\underset{\substack{\parallel \\ O}}{C}—NH(CH_2CH_2O)_n—X$$

where R' is a branched or straight chain aliphatic group having 8 to 18 carbon atoms, n is an integer of 4 to 100, and X is hydrogen, SO_3M, or PO_4M_2 where M is hydrogen or a bath-compatible cation such as Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb;

(b) 0.1 g./l. to 1 g./l. of at least one compound which is or which produces a chlorinated aromatic aldehyde of the formula



where n is 1 or 2;

(c) 0.25 g./l. to 5 g./l. of an aliphatic amine or a compound which produces an aliphatic amine; and

(d) 0.5 g./l. to 5 g./l. of an anti-oxidant or oxygen acceptor.

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. Using average current densities of 0.5 to 5.0 a.s.d., tin-lead alloy electrodeposits having average thicknesses of 0.25–25 microns may be obtained using plating times which may average 0.1–100 minutes.

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 bright 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 appearance, 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 following examples are submitted for the purpose of illustration only, so that those skilled in the art of tin-lead alloy 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.

PLATING TEST CONDITIONS

(A) Hull cell tests

Hull cell: plastic with a plating solution volume of 267 ml.
Anode: slab of Sn-Pb alloy (60% Sn and 40% Pb by weight)
Cathode: polished brass 10 cm. x 7.5 cm. x 1 mm. with 5 cm. immersed
Cell current: 1 ampere (0 to 7 a.s.d. range)
Time: minutes
Agitation: magnetic stirrer
Temperature: ambient room (20° C.–25° C.)

(B) Life tests—4 liter solution volume-strip cathodes

Plating cell: rectangular glass battery jar 15.5 cm. length, 13 cm. width, 26.5 cm. depth
Solution volume: 4 liters (solution depth of 20.5 cm.)
Anode: slab of Sn-Pb cast alloy (60% Sn and 40% Pb by weight) 9 cm. wide, 1 cm. thick, 20.5 cm. immersed in plating bath
Cathode: polished brass 20.4 cm. long, 2.54 cm. wide, 0.5 mm. thick immersed to depth of 18 cm.—maintained parallel to the anode at a distance of about 10 cm.—bottom of cathode bent to give an internal angle of 45° facing anode
Agitation: moving cathode bar—length of stroke 8 cm.—78 strokes/minute—total cathode travel 625 cm./minute
Temperature: ambient room (20° C.–25° C.)
Cell current: varied from 2 to 5 amperes
Time: varied from 3 minutes to several hours

(C) Barrel plating tests

Barrel: Plexiglas plastic of horizontal hexagonal type—12.5 cm. long with a diameter of about 10 cm.—completely immersed in plating bath—operated at 5 r.p.m.
Solution volume: 4 liters—cooled to compensate for heating effects of current by immersing in solution plastic cooling coils through which cold water circulated to maintain temperature at about 25° C.
Cell: polyethylene plastic
Load: steel nails about 5 cm. long with a total load area of about 930 square cm.
Current: varied from 5 to 25 amperes
Time: varied from 15 to 60 minutes

EXAMPLE 1

A stock solution was prepared having the following composition:

	G./l.
Stannous tin	52
Lead	30
Free fluoboric acid	100
Boric acid	25

To 267 ml. of the above stock solution, there were added the equivalent of

	G./l.
Tergitol Non-Ionic NP–35	10
Triton QS–15	10
o-Chlorbenzaldehyde	0.4

On running a Hull cell test as described in the above, a lustrous deposit was obtained throughout the entire current density range with a slight tendency toward striation or "ribbing" of deposit in the current density range of 2 to 7 a.s.d.

EXAMPLE 2

Example 1 was repeated using 0.4 g./l. of 2,6-dichlorobenzaldehyde in place of the o-chlorobenzaldehyde with essentially the same results obtained.

EXAMPLE 3

Example 1 was repeated using 0.4 g./l. of mi-chlorobenzaldehyde in place of the o-chlorobenzaldehyde with essentially the same results obtained.

EXAMPLE 4

A barrel plating test was run using the barrel plating conditions outlined in the above and using a cell current of 20 amperes for 30 minutes to give an average cathode current density of about 2 a.s.d. After plating the load of nails was rinsed and dried, and they had a beautifully lustrous and uniform appearance. On testing representative nails from the load the deposit ductility and adhesion to the basis metal was excellent. Because of the tumbling and some burnishing action no indication was obtained of any of the striation or "ribbing" effect indicated by the Hull Cell tests of Examples 1 to 3, inclusive.

The life test was continued for a total electrolysis time of about 300 ampere-hours with variations of current from 5 to 25 amperes per load and with times ranging from 15 minutes to 1 hour. Periodic replenishment of o-chlorobenzaldehyde easily maintained deposit luster with replenishment additions made on the basis of deposit appearance. Solderability tests were made on representative samples from a number of loads and the solderability was found to be excellent.

At the end of about 300 ampere-hours of electrolysis the bath was still performing excellently. A small amount of a white gelatinous sludge of basic stannic salts had precipitated out as would be expected from this type of bath due to some air oxidation of stannous tin, but the amount appeared tolerable and did not adversely affect bath performance.

EXAMPLE 5

To the bath of Example 1 there was added the equivalent of 2 g./l. of laurylamine. On repeating the Hull Cell test, the luster was unimpaired and in fact was more uniform and somewhat more reflective. However, no deposit striations or "ribbing" effects were now noticeable.

EXAMPLE 6

Example 5 was repeated using 2 g./l. octylamine in place of the laurylamine, with the same results obtained.

EXAMPLE 7

4 liters of solution were prepared having the following composition:

	G./l.
Stannous tin	55
Lead	25
Free fluoroboric acid	120
Boric acid	30
Tergitol Non-Ionic NP–35	10
Triton QS–15	10
o-Chlorobenzaldehyde	0.4
Laurylamine	2

Using conditions outlined under Life Tests supra, a brass cathode was plated for 15 minutes at 3 amperes to give an average cathode current density of about 3 a.s.d. The deposit was uniformly lustrous, ductile, and free of striations or "ribbing." The deposit also exhibited a remarkable degree of leveling as evidenced by the degree of obliteration of basis metal defects (pits, minor scratches, etc.) and the extraordinary smoothening of the rough sheared edges of the cathode.

The life test was continued for a total of 66 ampere-hours of electrolysis with periodic replenishment additions of o-chlorobenzaldehyde to maintain deposit luster. Plating times were varied from 3 minutes (which would give normally used thicknesses of alloy) to several hours and in general excellent deposits were still being obtained at the end of this electrolysis period. Deposit luster was easily maintaind with variations of current from 1 to 5 amperes per cathode and deposit ductility remained excellent.

An appreciable amount of a white gelatinous precipitate was formed during the electrolysis period due to air oxidation of stannous tin to stannic basic salts but the sludge had surprisingly little or no effect on the luster, smoothness and uniformity of deposits.

EXAMPLE 8

The Life Test of Example 7 was repeated using a freshly prepared bath but in addition adding as an anti-oxidant 1.5 g./l. hydroquinone. Excellent results were obtained as in Example 7 but after an electrolysis time of well over 100 ampere-hours the solution remained perfectly clear and free of any opalescence or any precipitate.

EXAMPLE 9

The Life Test of Example 7 was repeated using a freshly prepared bath but in addition adding as an antioxidant 0.2 g./l. of sodium benzene monosulfinate. Excellent results were obtained as in Example 7 but after an electrolysis time of well over 100 ampere-hours the solution remained perfectly clear and free of any opalescence or any precipitate.

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 for electrodepositing a bright, sound, smooth, ductile alloy of tin and lead which comprises passing current from an anode to a cathode through an aqueous acidic bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant of the formula

$$R''-\underset{\underset{O}{\|}}{C}-NH(CH_2CH_2O)_nX$$

where R'' is a branched or straight chain aliphatic group of 8 to 19 carbon atoms, *n* is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb; and

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

2. A process for electrodepositing a bright, sound, smooth, ductile alloy of tin and lead which comprises passing current from an anode to a cathode through an aqueous acidic bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant of the formula

$$R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-NH(C_2H_4O)_nSO_3Na$$

where R_1, R_2, and R_3 each exhibit 12 to 14 carbon atoms and *n* is about 15; and

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

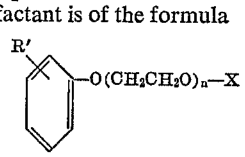
3. A process for electrodepositing a bright, sound, smooth, ductile alloy of tin and lead which comprises passing current from an anode to a cathode through an aqueous acidic bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant;

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent; and

(c) 0.25 g./l. to 5 g./l. of at least one aliphatic amine or a compound producing an aliphatic amine.

4. The process of claim **3** wherein at least one polyether surfactant is of the formula



where R' is an alkyl group of 8 to 20 carbon atoms, *n* is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb.

5. The process of claim **4** wherein at least one surfactant is a nonylphenol-ethylene oxide condensate exhibiting about 15 ethylene oxide groups per molecule.

6. The process of claim **3** wherein at least one polyether surfactant is of the formula

$$RO(CH_2CH_2-O)_n-X$$

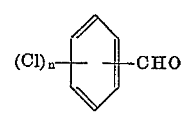
wherein R is a branched or straight chain aliphatic radical containing 4 to 18 carbon atoms, *n* is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb.

7. The process of claim **3** wherein at least one polyether surfactant is of the formula

$$R''-\underset{\underset{O}{\|}}{C}-NH(CH_2CH_2O)_nX$$

where R'' is a branched or straight chain aliphatic group of 8 to 18 carbon atoms, *n* is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb.

8. The process of claim **3** wherein said aromatic aldehyde produced is of the formula



where *n* is 1 to 2.

9. The process of claim **3** wherein the water soluble stannous tin salt is stannous fluoborate and the water soluble lead salt is lead fluoborate.

10. The process of claim **3** wherein said tin-lead alloy is about 60% tin and about 40% lead.

11. The process of claim **3** wherein said polyether surfactant is of the formula

$$R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-NH(C_2H_4O)_nSO_3Na$$

where R_1, R_2, and R_3 each exhibit 12 to 14 carbon atoms and *n* is about 15.

12. The process of claim **3** wherein said compound which is or which produces an aliphatic amine is selected from the group consisting of RNH_2 and

$$R-N=C\begin{matrix} \diagup R' \\ \diagdown R'' \end{matrix}$$

wherein R is a straight or branched chain alkyl group exhibiting 3 to 20 carbon atoms, R' and R'' are hydrogen, alkyl groups, or aromatic groups.

13. The process of claim **3** wherein said aliphatic amine is laurylamine.

14. The process of claim **3** wherein said aliphatic amine is octylamine.

15. A process for electrodepositing a bright, sound, smooth, ductile alloy of tin and lead which comprises passing current from an anode to a cathode through an aqueous acidic bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant;

(b) 0.1 g./l. to 1 g./l. of at least one compound which is or which produces an aromatic aldehyde exhibiting at least one chloro substituent;

(c) 0.25 g./l. to 5 g./l. of at least one compound which is or which produces an aliphatic amine; and

(d) 0.5 g./l. to 5 g./l. of at least one anti-oxidant or oxygen acceptor to maintain tin in its divalent stannous form.

16. The process of claim **15** wherein said anti-oxidant compound is an aromatic sulfinate.

17. The process of claim **16** wherein said aromatic sulfinate is sodium benzene monosulfinate.

18. The process of claim **15** wherein said anti-oxidant compound is hydroquinone or substituted hydroquinone.

19. The process of claim **15** wherein said anti-oxidant compound is pyrocatechol.

20. The process of claim **15** wherein said anti-oxidant compound is catechol.

21. The process of claim **15** wherein said anti-oxidant compound is pyrogallol.

22. A process for electrodepositing a bright, sound, smooth, ductile alloy of tin and lead having about 60% tin and about 40% lead comprising passing current from an anode to a cathode through an aqueous acidic bath containing 110 g./l. to 135 g./l. of stannous fluoborate; 37 g./l. to 55 g./l. of lead fluoborate; 100 g./l. to 200 g./l. of fluoboric acid; 10 g./l. to 40 g./l. of boric acid; and as a novel additive system:

(a) at least 1 g./l. of at least one polyether surfactant selected from the group consisting of

$$R—(CH_2CH_2—O)_n—X$$

where R is an aliphatic alcohol moiety R′—O— where R′ is an aliphatic radical containing 4 to 18 carbon atoms or an aromatic alcohol moiety

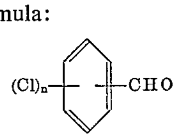
where R″ is an aliphatic radical containing 8 to 20 carbon atoms;

$$R'NH(CH_2CH_2O)_n—X$$

$$R'—\underset{\underset{O}{\|}}{C}—NH(CH_2CH_2O)_n—X$$

where R′ is a branched or straight chain aliphatic group having 8 to 18 carbon atoms, n is an integer of 4 to 100, and X is hydrogen, SO_3M, or PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb;

(b) 0.1 g./l. to 1 g./l. of at least one compound which is or which produces a chlorinated aromatic aldehyde of the formula:



where n is 1 or 2;

(c) 0.25 g./l. to 5 g./l. of a compound which is or which produces an aliphatic amine; and

(d) 0.5 g./l. to 5 g./l. of an anti-oxidant or oxygen acceptor to maintain tin in its divalent stannous form.

23. A composition for producing bright, sound, smooth, ductile tin-lead alloy electrodeposits which comprises an aqueous acidic bath composition containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant of the formula

$$R''—\underset{\underset{O}{\|}}{C}—NH(CH_2CH_2O)_nX$$

wherein R″ is a branched or straight chain aliphatic group of 8 to 18 carbon atoms, n is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb; and

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

24. A composition for producing bright, sound, smooth, ductile tin-lead alloy electrodeposits which comprises an aqueous acidic bath composition containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant of the formula

$$R_2—\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}—NH(C_2H_4O)_nSO_3Na$$

where R_1, R_2, and R_3 each exhibit 12 to 14 carbon atoms and n is about 15; and

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent.

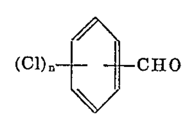
25. A composition for producing bright, sound, smooth, ductile tin-lead alloy electrodeposits which comprises an aqueous plating bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least 1 g./l. of at least one polyether surfactant;

(b) 0.1 g./l. to 1 g./l. of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent; and

(c) 0.25 g./l. to 5 g./l. of at least one aliphatic amine or a compound producing an aliphatic amine.

26. The composition of claim **25** wherein said aromatic aldehyde produced is of the formula



where n is 1 to 2.

27. The composition of claim **26** wherein at least one surfactant is a nonylphenol-ethylene oxide condensate exhibiting about 15 ethylene oxide groups per molecule.

28. The composition of claim **25** wherein the water soluble stannous tin salt is stannous fluoborate and the water soluble lead salt is lead fluoborate.

29. The composition of claim **28** wherein said polyether surfactant is of the formula

$$R_2—\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}—NH(C_2H_4O)_nSO_3Na$$

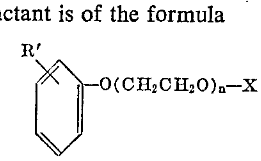
wherein R_1, R_2, and R_3 each exhibit 12 to 14 carbon atoms and n is about 15.

30. The composition of claim **25** wherein at least one polyether surfactant is of the formula

$$RO(CH_2CH_2)_n—X$$

wherein R is a branched or straight chain aliphatic radical containing 4 to 18 carbon atoms, n is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2 ,Sn_2, Ca_2, Cs, or Rb.

31. The composition of claim **25** wherein at least one polyether surfactant is of the formula



wherein R′ is an alkyl group of 8 to 20 carbon atoms, n is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sb_2, Ca_2, Cs, or Rb.

32. The composition of claim **26** wherein at least one polyether surfactant is of the formula

$$R''-\underset{\underset{O}{\|}}{C}-NH(CH_2CH_2O)_nX$$

where R'' is a branched or straight chain aliphatic group of 8 to 18 carbon atoms, *n* is an integer 4 to 100, and X is selected from the group consisting of hydrogen, SO_3M, and PO_4M_2 where M is hydrogen or a bath-compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb.

33. The composition of claim **25** wherein said tin-lead alloy is about 60% tin and about 40% lead.

34. The composition of claim **25** wherein said compound which is or which produces an aliphatic amine is selected from the group consisting of RNH_2 and

$$R-N=C\begin{matrix}R^1\\R''\end{matrix}$$

wherein R is a straight or branched chain alkyl group exhibiting 3 to 20 carbon atoms, R' and R'' are hydrogen, alkyl groups or aromatic groups.

35. The composition of claim **25** wherein said aliphatic amine is laurylamine.

36. The composition of claim **25** wherein said aliphatic amine is octylamine.

37. A composition for producing bright, sound, smooth, ductile tin-lead alloy electrodeposits which comprises an aqueous acidic plating bath containing at least one water soluble stannous tin salt, at least one water soluble lead salt, and as cooperating additives:

(a) at least **0.1** g./l. of at least one polyether surfactant;
(b) 0.1 g./l. to 1 g./l of at least one aromatic aldehyde exhibiting at least one chloro substituent or at least one compound producing an aromatic aldehyde exhibiting at least one chloro substituent;
(c) 0.25 g./l. to 5 g./l. of at least one aliphatic amine or a compound producing an aliphatic amine; and
(d) 0.5 g./l. to 5 g./l. of at least one anti-oxidant or oxygen acceptor to maintain tin in its divalent stannous form.

38. The composition of claim **37** wherein said anti-oxidant compound is an aromatic sulfinate.

39. The composition of claim **38** wherein said aromatic sulfinate is sodium benzene monosulfinate.

40. The composition of claim **37** wherein said anti-oxidant compound is hydroquinone or substituted hydroquinone.

41. The composition of claim **37** wherein said anti-oxidant compound is pyrocatechol.

42. The composition of claim **37** wherein said anti-oxidant compound is catechol.

43. The composition of claim **37** wherein said anti-oxidant compound is pyrogallol.

44. A composition for producing a bright, sound, smooth, ductile electrodeposit of an alloy of tin and lead having about 60% tin and about 40% lead which comprises an aqueous acidic bath containing gas components 110 g./l. to 135 g./l. of stannous fluoborate, 37 g./l. to 55 g./l. of lead fluoborate; 100 g./l. to 200 g./l. of fluoboric acid; 10 g./l. to 40 g./l. of boric acid; and as a novel additive system:

(a) at least 1 g./l. of at least one polyether surfactant selected from the group consisting of

$$R-(CH_2CH_2-O)_n-X$$

where R is an aliphatic alcohol moiety R'—O— where R' is an aliphatic radical containing 4 to 18 carbon atoms or an aromatic alcohol moiety

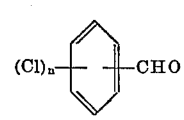
where R'' is an aliphatic radical containing 8 to 20 carbon atoms;

$$R'NH(CH_2CH_2O)_n-X$$

$$R'-\underset{\underset{O}{\|}}{C}-NH(CH_2CH_2O)_n-X$$

where R' is a branched or straight chain aliphatic group having 8 to 18 carbon atoms, *n* is an integer of 4 to 100, and X is hydrogen, SO_3M, or PO_4M_2 where M is hydrogen or a bath compatible cation comprising Na, K, NH_4, Mg, Pb_2, Sn_2, Ca_2, Cs, or Rb;

(b) 0.1 g./l. to 1 g./l. of at least one compound which is or which produces a chlorinated aromatic aldehyde of the formula



where *n* is 1 or 2;

(c) 0.25 g./l. to 5 g./l. of a compound which is or which produces an aliphatic amine; and
(d) 0.5 g./l. to 5 g./l. of an anti-oxidant or oxygen acceptor.

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