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ELECTROPLATING BATH FOR DEPOSITING TIN-LEAD ALLOY PLATES

Friedrich Sedlacek and Joachim Korpiun, Geislingen, Steige, Germany, assignors to Dr.-Ing. Max Schloetter, Fabrik fuer Galvanotechnik, Geislingen, Steige, Germany

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U.S. Cl. 204—43 18 Claims

ABSTRACT OF THE DISCLOSURE

Semibright to bright deposits of tin-lead alloys on articles are produced by electroplating the articles with an electroplating bath comprising a tin compound, a lead compound, preferably the fluoborates of stannous tin and plumbous lead, fluoboric acid, boric acid, a wetting agent, and, as brightening agent, a methylene aniline compound or a diamino diphenylmethane compound, preferably in combination with a brightener as conventionally used in electroplating tin baths.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to an electroplating solution or bath and more particularly to a bath for depositing semi-bright to fully bright plates or coatings of a tin-lead alloy, to an electroplating process by means of such a bath, and to articles obtained by electroplating in such a bath, said articles being coated with a tin-lead alloy.

(2) Description of the prior art

Electrolytes for the galvanic electrodeposition of coatings of tin-lead alloys are known. The electrolytes used heretofore for this purpose contain lead and bivalent tin in the form of their fluoborates and in addition thereto, free fluoboric acid, boric acid, and organic additives for leveling the deposited alloy. The heretofore known and used organic additives, however, yield only dull tin-lead alloy plates or at the most such plates of silky appearance. However, the need exists in the electronics industry to produce tin-lead alloy plates of bright appearance.

SUMMARY OF THE INVENTION

Now it is one object of the present invention to provide an electroplating bath for depositing tin-lead alloy plates of a satisfactory brightness.

Another object of the present invention is to provide a simple and effective electroplating process whereby bright to fully bright deposits of tin-lead alloys are produced under economic conditions.

Still another object of the present invention is to provide articles of bright appearance which have been electroplated with a tin-lead alloy.

Other objects of the present invention and advantageous features thereof will become apparent as the description proceeds.

In principle, the present invention comprises adding to an aqueous electrolyte which contains lead and bivalent tin in the desired predetermined proportion, said lead and bivalent tin being present in the form of their fluoborates, free fluoboric acid, if desired, also boric acid, furthermore wetting agents, and formaldehyde, and as novel brightening agents, amino compounds of Formula I:

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—X_2 \quad (I)$$

In said formula

X_1 is either hydrogen or the



group;

X_2 is either hydrogen or the



group;

R_1 and R_2 are hydrogen, alkyl with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, alkynyl with 2 to 4 carbon atoms;

R_3 and R_4 are hydrogen or alkyl with 1 to 3 carbon atoms;

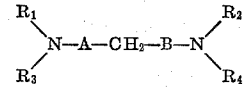
A and B are phenylene or phenylene substituted by alkyl with 1 to 3 carbon atoms or by halogen; and

m is 1 of the numerals 0 and 1, whereby if m is 1, X_1 and X_2 are hydrogen.

The preferred compounds of this formula are those of group A as indicated by Formula II:

$$A—NR_1—CH_2—NR_2—B \quad (II)$$

Likewise compounds of group B as indicated by Formula III have proved to be useful:



(III)

Additives of Formulas I, II, and III have a brightening effect depending on the type of the substituents designated by R_1, R_2, R_3, and R_4 at concentrations from about 0.05 g./liter to about 5.0 g./liter of electrolyte. Preferred concentrations for optimum effects are between about 0.1 g./liter and about 2.0 g./liter.

The brightening additives according to the present invention as illustrated by the above given formulas are used in any known lead-tin alloy plating bath. Such baths are useful, for instance, for solderability in the 50:50 lead/tin range.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples serve to illustrate the present invention without, however, being limited thereto. *The basic electroplating Bath A* as used in the following Examples 1 to 7 operates at a cathodic current density of 2 amp./sq. dm. and at an electrolyte temperature of 20–25° C. Thereby coatings of tin-lead alloy with a tin content of 60 to 65% are deposited. It is, of course, also possible to vary the tin content of the deposited alloy plates to a considerable extent by varying the concentration of the lead and tin ions in the electrolyte. Thereby, the proportion of lead to tin in the electrolyte is of importance. If the tin concentration is increased relative to the lead concentration, plates with a higher tin content are obtained, and vice versa. These rules correspond to the theory of electrolytic deposition of alloys.

It was found that the appearance of the deposits as obtained according to the following examples is rarely changed if the tin content of the deposited alloy plates varies between about 40% and about 80%. An alloy containing about 60% of tin is preferably strived for because it corresponds to the composition of soldering tin. *Basic electroplating Bath A,* as used in the following Examples 1 to 7, contains:

9.2 g./liter of stannous tin in the form of the fluoborate;
4.3 g./liter of plumbous lead in the form of its fluoborate;
230 g./liter of free 50% fluoboric acid;
10 g./liter of boric acid;
12 g./liter of the condensation product of nonyl phenol with 14 moles of ethylene oxide as wetting agent;
10 g./liter of a 38% formaldehyde solution.

Electroplating is carried out in all examples for 15 minutes.

EXAMPLE 1

0.5 g./liter of 4,4'-diaminodiphenylmethane are added to Bath A. Uniformly bright tin-lead plates which show a somewhat hazy luster are obtained.

EXAMPLE 2

0.3 g./liter of 4,4'-bis-(N-monoethylamino) diphenylmethane added to Bath A yield bright tin-lead alloyed plates which show a somewhat stronger haziness than the electroplated articles obtained according to Example 1.

EXAMPLE 3

0.1 g./liter of 4,4'-bis-(N-diethylamino) diphenylmethane are added to Bath A. The same results are obtained as in Example 2.

EXAMPLE 4

0.2 g./liter of methylene-bis-aniline are added to Bath A. Bright but somewhat hazy plates of about the same appearance as those obtained according to Example 1 are produced.

EXAMPLE 5

0.2 g./liter of methylene-bis-(N-methylaniline) produce about the same results as obtained according to Example 4.

EXAMPLE 6

0.2 g./liter of methylene-bis-(N-ethyl-p-toluidine) are added to Bath A. Uniformly bright, slightly hazy tin-lead plates are deposited.

EXAMPLE 7

1.0 g./liter of methylene-bis-(N-propargylaniline) are added to Bath A. Bright deposits with only a slight haze are obtained.

The tin-lead alloy plates deposited according to the preceding Examples 1 to 7 can readily be soldered and retain this property even on storage for a prolonged period of time. If larger surfaces electroplated with such a lead-tin alloy according to the preceding examples, are heated to a temperature at which the alloy melts, i.e. to about 190–200° C., the melt covers uniformly the entire metal surface. Electrolytically deposited bright plates which consist solely of pure tin and which may have a similar or even better brightness than the tin-lead alloy plates obtained according to Examples 1 to 7, show, on melting, the disadvantage in contrast to the tin-lead alloy plates according to the present invention, that the liquefied tin runs together and forms a few drops but does not uniformly coat the surface. This behavior, of course, is quite undesirable. Thus in this respect bright or fully bright electroplated tin-lead alloys deposits according to the present invention have a distinct advantage over bright electroplated tin plates.

The degree of brightness of the tin-lead alloy plates deposited according to the present invention can further be increased by adding to the electrolyte compounds which are known to act as brighteners in electrolytes used for depositing pure tin. The compounds which are used for this purpose are derived from various groups of compounds and of these the following have been tested and all of them have been found to be effective. Preferred compounds of this type are unsaturated carbonyl compounds such as, for instance,

Benzalacetone,
cinnamic aldehyde,
2,3-dihydrobenzaldehyde,
thiophene aldehyde,
furfural,
furfurylidene acetone,
2-methyl-2,3-dihydrobenzaldehyde,
2-acetyl furane.

The present invention, however, is not limited to the above mentioned brighteners used in electrodepositing tin plates since other known agents suitable for this purpose can also be employed. Simple tests will show which brightener can be used in electroplating baths according to the present invention.

The range of effectiveness of these additives to the electroplating baths according to the present invention is dependent upon the compound used and is between about 0.03 g./liter and about 3.0 g./liter of electrolyte. Preferably amounts of about 0.05 g./liter and about 2 g./liter of electrolyte are used for achieving optimum results.

When adding such brighteners as they are known for depositing tin plates alone as additives to tin-lead alloy electrolytes, the deposited tin-lead alloy plates show also a certain hazy or cloudy brightness which, however, does not at all exceed the effect of the compounds according to the present invention and which, in many instances, does not even match said effect. However, when adding the compounds according to the present invention of Formula I as well as the brighteners as they are known for depositing pure bright tin plates, a surprisingly advantageous synergistic effect of the combination of these two brightening agents is achieved. It is entirely unexpected that the addition of two compounds each of which produces in tin-lead alloy plates no sufficiently satisfactory brightness but only hazy luster, will yield fully bright plates when used together.

The following examples illustrate the combinations of the known brighteners as used for depositing tin plates with the additives of Formula I according to the present invention without, however, being limited thereto.

The composition of the *basic electroplating Bath B* as used in the following examples is as follows:

11.2 g./liter of stannous tin in the form of its fluoborate,
5.2 g./liter of plumbous lead in the form of its fluoborate,
300 g./liter of free 50% fluoboric acid,
10 g./liter of boric acid,
12 g./liter of the condensation product of dodecylphenol with 12 moles of ethylene oxide as wetting agent,
15.0 g./liter of 38% formaldehyde solution.

EXAMPLE 8

0.12 g./liter of methylene-bis-aniline and
0.07 g./liter of cinnamic aldehyde

are added to Bath B. On electroplating with such an electrolyte at a bath temperature of 20–22° C. and a current density of 2–3 amp./sq.dm., a clear bright tin-lead alloy deposit is produced. The result is always the same even when electroplating at shorter or longer deposition times. For technical purposes times of exposure to the electrolyte which vary from 10 minutes to 20 minutes, are used.

EXAMPLE 9

0.1 g./liter of 4,4'-diamino diphenylmethane and
0.04 g./liter of 2-methyl-2,3-dihydrobenzaldehyde

are added to Bath B.

EXAMPLE 10

1.0 g./liter of methylene-bis-aniline and
0.08 g./liter of thiophene aldehyde

are added to Bath B.

According to Examples 9 and 10 clear bright tin-lead alloy plates are obtained under the above given working conditions.

Basic electroplating Bath C as used in the following examples is composed as follows:

8.0 g./liter of stannous tin in the form of its fluoborate,
3.8 g./liter of plumbous lead in the form of its fluoborate,
250 g./liter of free 50% fluoboric acid,
10 g./liter of boric acid,
12 g./liter of the condensation product of nonyl phenol with 16 moles of ethylene oxide, as wetting agent, and
12 g./liter of 38% formaldehyde solution.

EXAMPLE 11

0.1 g./liter of methylene-bis-aniline and
0.05 g./liter of 2,3-dihydrobenzaldehyde

are added to Bath C.

EXAMPLE 12

0.7 g./liter of methylene-bis-(N-methylaniline) and
0.16 g./liter of furfurylidene acetone

are added to Bath C.

A clear bright tin-lead alloy plate is produced according to Examples 11 and 12 under the above given conditions.

The following examples are carried out with *the basic electroplating Bath D* of the following composition:

9.2 g./liter of stannous tin in the form of its fluoborate,
4.3 g./liter of plumbous lead in the form of its fluoborate,
260 g./liter of free 50% fluoboric acid,
10 g./liter of boric acid,
12 g./liter of the condensation product of undecyl phenol with 16 moles of ethylene oxide as wetting agent.

The working temperature in the following examples is between 20° C. and 24° C.

EXAMPLE 13

20 g./liter of a 38% formaldehyde solution,
0.3 g./liter of 4,4'-diethylamino diphenylmethane, and
0.09 g./liter of furfural

are added to Bath D.

Electroplating with a current density of 2–3 amp./sq.-dm. yields fully bright tin-lead alloy plates.

EXAMPLE 14

20 g./liter of 38% formaldehyde solution,
0.5 g./liter of 4,4' - bis - (N - n-propylamino) diphenylmethane, and
0.27 g./liter of 2-acetylfurane

are added to Bath D.

On operating with current densities of 3–4 amp./sq.dm. fully bright tin-lead alloy plates are obtained.

EXAMPLE 15

30 g./liter of a 38% formaldehyde solution,
0.4 g./liter of methylene-bis-(N-ethyl-p-toluidine), and
0.27 g./liter of 2-acetylfurane

are added to Bath D.

On operating with current densities of 2.5–3.5 amp./sq.dm. fully bright tin-lead alloy plates are deposited.

EXAMPLE 16

15 g./liter of a 38% formaldehyde solution,
0.7 g./liter of 4,4'-bis-(N-diethylamino) diphenylmethane, and
0.3 g./liter of benzalacetone

are added to Bath D.

EXAMPLE 17

12 g./liter of 38/ formaldehyde solution,
0.7 g./liter of methylene-bis-(N-allylaniline), and
0.4 g./liter of benzalacetone

are added to Bath D.

EXAMPLE 18

0.4 g./liter of methylene-bis-aniline and
0.3 g./liter of benzalacetone

are added to Bath A.

EXAMPLE 19

0.3 g./liter of 4,4'-diamino diphenylmethane and
0.4 g./liter of benzalacetone

are added to Bath A.

EXAMPLE 20

0.2 g./liter of methylene-bis-(N-n-propylaniline) and
0.3 g./liter of benzalacetone

are added to Bath A.

EXAMPLE 21

1.0 g./liter of methylene bis-(N-propargylaniline) and
0.4 g./liter of benzalacetone

are added to Bath A.

EXAMPLE 22

0.7 g./liter of methylene-bis-(N-ethyl aniline) and
0.2 g./liter of benzalacetone

are added to Bath A.

When operating at 20–24° C. with current densities of 1.5–3.0 amp./sq./dm. with the electrolytes as given in Examples 16 to 22, fully bright tin-lead alloy deposits are produced.

There is a great choice of non-ionogenic, surface-active polyoxy ethylene compounds added as wetting agents to the electroplating baths so that a large number of such compounds are available for such addition. The preferred compounds are those in which at least 6 ethylene oxide groups are condensed with long-chain fatty alcohols, long-chain fatty acids, long-chain fatty amines, or long-chain alkyl phenols. The term "Long-chain" indicates molecules which contain at least 6 carbon atoms. Frequently it is advisable to select compounds with 10 or more, up to 30 oxyethylene groups in their molecule in order to provide good water solubility. Nonyl phenol reacted with about 15 moles of ethylene oxide yields, for instance, an especially valuable wetting agent. Other ethylene oxide condensation products of higher alkyl phenols which contain 8 to 15 carbon atoms at the alkyl substituent also produce excellent results. Such products are non-ionogenic wetting agents. Sulfated compounds of this type can also be used for the purpose of the present invention.

The tin-lead alloy plates produced according to Examples 8 to 22 have the advantage over bright deposits of tin plates produced according to known processes that they uniformly coat even larger surface areas when molten and that they do not run together to form drops.

In place of the brightening bis-(phenylamino) methane compounds or diamino diphenyl methane compounds used in the preceding examples, there can also be added corresponding amounts of the following agents while otherwise the procedure is the same as described therein:

4,4'-bis-(N-methylamino) diphenylmethane,
4,4'-bis-(N-dimethylamino) diphenylmethane,
4,4'-bis-(N-ethylamino) diphenylmethane,
4,4'-bis-(N-n-butylamino) diphenylmethane,
4,4'-diamino-3,3'-dimethyl diphenylmethane,
4,4'-diamino-3,3'-dichloro diphenylmethane,
methylene bis-(p-chloro aniline),
methylene bis-xylidine,

methylene bis-(N-methyl-p-toluidine),
methylene bis-p-toluidine,

and the like compounds.

The lead and tin content of the resulting lead-tin alloy deposits may be between about 5% and about 90% of lead and accordingly between about 95% and about 10% of tin depending upon the composition of the electrolyte. The process can be used for electropltaing structural units of any type, sheet metals, wire materials, and articles made therefrom, especially construction elements useful in the electronics industry.

The preferred electroplating baths according to the present invention are composed as follows:

10 g./liter to 50 g./liter of stannous tin and plumbous lead in the form of their fluoborates,
50 g./liter to 400 g./liter of free 50% fluoboric acid,
10 g./liter to 40 g./liter of free boric acid,
5 g./liter to 20 g./liter of the wetting agent, preferably of an alkyl aryl ether such as the condensation product of nonyl phenol with 14 moles of ethylene oxide,
5 g./liter to 30 g./liter of 38% formaldehyde solution,
0.1 g./liter to 2.0 g./liter of the brightening agent according to the present invention, such as methylene bis-N-ethylaniline), and
0.05 g./liter to 0.50 g./liter of an unsaturated carbonyl compound, such as benzal acetone.

The current density which can be achieved is dependent upon the metal content of the bath and is between 1 amp./sq. dm. and 10 amp./sq. dm.

Especially good results are obtained with electroplating baths of the following composition:

12 g./liter to 15 g./liter of stannous tin and plumbous lead in the form of their fluoborates,
200 g./liter to 260 g./liter of free 50% fluoboric acid,
10 g./liter to 12 g./liter of free boric acid,
11 g./liter to 13 g./liter of a wetting agent,
10 g./liter to 15 g./liter of 38% formaldehyde solution,
0.6 g./liter to 0.8 g./liter of the brightening agent according to the present invention, and
0.1 g./liter to 0.4 g./liter of the carbonyl compound.

The current density which can be achieved with such an electroplating bath is between 1.5 amp./sq. dm. and 2.0 amp./sq. dm.

The anodes used in the electroplating baths according to the present invention are preferably composed of tin-lead alloys of a composition corresponding to the desired tin-lead alloy plate. Thus if a deposit of 60% tin and 40% lead is to be produced, anodes of the same tin and lead content are employed. The thickness of the deposits can be between about 2μ and about 20μ. It depends in principle upon the subsequently applied method of soldering. For melt soldering a plate thickness of 6μ to 8μ and for drag soldering a plate thickness of 5μ to 20μ has proved to be satisfactory. Subsequent treatment of the resulting plates on the electroplated articles is not necessary.

It may be mentioned that the lead-tin alloy plates provide a more stable corrosion protection than the single tin or lead plates and are also harder than the latter. Small articles as they are used in precision mechanical work and the electroindustry, which are to be soft-soldered, contain, for instance, an alloy of 15% to 35% of tin and 85% to 65% of lead. In the precision mechanical industry and the electroindustry such a tin-lead alloy deposit results in a better appearance of the solder.

Of course, many changes and variations in the diamino diphenyl methane compounds of Formula III and the methylene-bis-aniline compounds of Formula II, the non-ionogenic surface active polyoxyethylene compounds and other wetting agents, and the additives known and heretofore used as brighteners in tin electroplating baths, in the amounts of the above components and additives present in such baths, in the current densities and bath temperature observed during electroplating, and the like may be made by those skilled in the art in accordance with the principles set forth herein and in the claims annexed hereto.

We claim:

1. An electroplating bath for depositing bright lead-tin alloy plates, said bath comprising an aqueous solution of
stannous fluoborate,
plumbous fluoborate,
free fluoboric acid,
free boric acid,
a wetting agent compatible with the bath components, formaldehyde, and

as brightening agent, a compound of the formula

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—X_2$$

wherein

X_1 is a member selected from the group consisting of hydrogen and the amino group of the formula



X_1 is a member selected from the group consisting of hydrogen and the amino group of the formula



A and B are members selected from the group consisting of phenylene, phenylene substituted by alkyl with 1 to 3 carbon atoms, and phenylene substituted by halogen;
R_1 and R_2 are members selected from the group consisting of hydrogen, alkyl with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, and alkynyl with 2 to 4 carbon atoms;
R_3 and R_4 are members selected from the group consisting of hydrogen and alkyl with 1 to 3 carbon atoms; and
m is one of the numerals 0 and 1, whereby, if *m* is 1, X_1 and X_2 are hydrogen.

2. The electroplating bath of claim **1**, in which additional compounds serving as brightening agents in baths for depositing bright tin deposits are added to the electroplating bath.

3. The electroplating bath of claim **2**, in which the brightening compound additionally added to the bath is a carbonyl compound selected from the group consisting of
cinnamic aldehyde,
thiophene aldehyde,
furfural,
furfurylidene acetone,
2-acetylfurane,
2,3-dihydrobenzaldehyde,
2-methyl-2,3-dihydrobenzaldehyde, and
benzal acetone,

4. The electroplating bath of claim **2**, in which the brightening compound additionally added to the bath is an unsaturated carbonyl compound.

5. The electroplating bath of claim **1**, in which the wetting agent is the condensation product of an alkyl phenol, the alkyl substitutent thereof having 8 to 15 carbon atoms, with 6 to 30 moles of ethylene oxide.

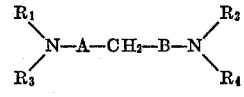
6. The electroplating bath of claim **5**, in which the condensation product of an alkyl phenol with ethylene oxide is the condensation product of nonyl phenol with 12 to 16 moles of ethylene oxide.

7. The electroplating bath of claim 1, in which the brightening agent is a compound of the formula

$$A—NR_1—CH_2—NR_2—B$$

in which formula A, B, R_1, and R_2 are the members indicated in claim 1.

8. The electroplating bath of claim 1, in which the brightening agent is a compound of the formula



in which formula A, B, R_1, R_2, R_3, and R_4 are the members indicated in claim 1.

9. The electroplating bath of claim 1, in which the brightening agent is present in the electroplating bath in an amount between about 0.05 g./liter and about 5.0 g./liter.

10. The electroplating bath of claim 1, in which the brightening agent is present in the electroplating bath in an amount between about 0.1 g./liter and about 2.0 g./liter.

11. The electroplating bath of claim 1, in which the brightening agent is a compound selected from the group consisting of

4,4'-diamino diphenylmethane,
4,4'-bis-(N-methylamino) diphenylmethane,
4,4'-bis-(N-dimethylamino) diphenylmethane,
4,4'-bis-(N-ethylamino) diphenylmethane,
4,4'-bis-(N-diethylamino) diphenylmethane,
4,4'-bis-(N-n-propylamino) diphenylmethane,
4,4'-bis-(N-propargylamino) diphenylmethane,
4,4'-bis-(N-n-butylamino) diphenylmethane,
4,4'-diamino-3,3'-dimethyl diphenylmethane, and
4,4'-diamino-3,3'-dichloro diphenylmethane.

12. The electroplating bath of claim 1, in which the brightening agent is a compound selected from the group consisting of

methylene bis-aniline,
methylene bis-(N-methylaniline),
methylene bis-(N-ethylaniline),
methylene bis-(N-n-propylaniline),
methylene bis-(N-propargylaniline),
methylene bis-xylidine,
methylene bis-(N-ethyl-p-toluidine),
methylene (bis-N-methyl-p-toluidine),
methylene bis-p-toluidine, and
methylene bis-p-chloroaniline.

13. The electroplating bath of claim 1, in which the wetting agent is an alkyl aryl ether having 6 to 30 oxyethylene groups (C_2H_4O-groups) in its molecule.

14. The electroplating bath of claim 1, said bath containing per liter

10 g. to 50 g. of stannous tin and plumbous lead in the form of their fluoborates,
50 g. to 400 g. of free 50% fluoboric acid,
10 g. to 40 g. of free boric acid,
5 g. to 20 g. of the wetting agent,
5 g. to 30 g. of 38% formaldehyde solution,
0.1 g. to 2.0 g. of the brightening agent of the formula

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—X_2$$

wherein

X_1, X_2, A, B, R_1, R_2 and m represent the same members and numerals as given in claim 1, and
0.05 to 0.50 g. of an unsaturated carbonyl compound.

15. The electroplating bath of claim 1, said bath containing per liter

12 g. to 15 g. of stannous tin and plumbous lead in the form of their fluoborates,
200 g. to 260 g. of free 50% fluoboric acid,
10 g. to 12 g. of free boric acid,
11 g. to 13 g. of the wetting agent,
10 g. to 15 g. of 38% formaldehyde solution,
0.6 g. to 0.8 g. of the brightening agent of the formula

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—X_2$$

wherein

X_1, X_2, A, B, R_1, R_2 and m represent the same members and numerals as given in claim 1, and
0.1 g. to 0.4 g. of an unsaturated carbonyl compound.

16. In a process of electroplating articles and depositing thereon a bright tin-lead alloy plate deposit, the step which comprises

(a) preparing the electroplating bath of claim 1,
(b) immersing the article to be provided with a tin-lead alloy plate in said bath, and
(c) applying a potential across the anode and the article to deposit a tin-lead alloy plate on said article.

17. In a process of electroplating articles and depositing thereon a bright tin-lead alloy plate deposit, the step which comprises

(a) preparing the electroplating bath comprising an aqueous solution of
stannous fluoborate,
plumbous fluoborate,
free fluoboric acid,
free boric acid,
a wetting agent compatible with the bath components,
formaldehyde, and
as brightening agent, a compound of the formula

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—(X_2)_n$$

wherein

X_1 is a member selected from the group consisting of hydrogen and the amino group of the formula



X_2 is a member selected from the group consisting of hydrogen and the amino group of the formula



A and B are members selected from the group consisting of phenylene, phenylene substituted by alkyl with 1 to 3 carbon atoms, and phenylene substituted by halogen;
R_1 and R_2 are members selected from the group consisting of hydrogen, alkyl with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, and alkynyl with 2 to 4 carbon atoms;
R_3 and R_4 are members selected from the group consisting of hydrogen and alkyl with 1 to 3 carbon atoms; and
m is one of the numerals 0 and 1, whereby, if m is 1, X_1 and X_2 are hydrogen,

(b) immersing the article to be provided with a bright tin-lead alloy plate in said bath, and
(c) applying a potential across the anode and the article to deposit a tin-lead alloy plate on said article.

18. An electroplating bath for depositing bright lead-in alloy plates, said bath comprising an aqueous solution of

stannous fluoroborate,
plumbous fluoborate,
free fluoboric acid,
a wetting agent compatible with the bath components,
formaldehyde, and

as brightening agent, a compound of the formula

$$X_1—A—(NR_1)_m—CH_2—(NR_2)_m—B—X_2$$

wherein

X_1 is a member selected from the group consisting of hydrogen and the amino group of the formula



X_2 is a member selected from the group consisting of hydrogen and the amino group of the formula



A and B are members selected from the group consisting of phenylene, phenylene substituted by alkyl with 1 to 3 carbon atoms, and phenylene substituted by halogen;

R_1 and R_2 are members selected from the group consisting of hydrogen, alkyl with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, and alkynyl with 2 to 4 carbon atoms;

R_3 and R_4 are member selected from the group consisting of hydrogen and alkyl with 1 to 3 carbon atoms, and

m is one of the numerals 0 and 1, whereby, if *m* is 1, X_1 and X_2 are hydrogen.

References Cited

UNITED STATES PATENTS

3,554,878	1/1971	Rothschild	204—43 X
2,846,381	8/1958	Frick et al.	204—54 R
3,471,379	10/1969	Schoot et al.	204—54 R

FOREIGN PATENTS

1,151,460	5/1969	Great Britain	204—43
1,089,479	11/1967	Great Britain	204—54 R

GERALD L. KAPLAN, Primary Examiner