United States Patent Office 2,734,025 Patented Feb. 7, 1956

2,734,025

LEAD-TIN ALLOY PLATING

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No Drawing. Application February 4, 1954, Serial No. 408,296

29 Claims. (Cl. 204—43)

This application is a continuation-in-part of my co-pending application Serial No. 290,333, filed May 27, 1952.

This invention relates to a process for the electrodeposition of alloys of lead and tin, baths therefor, and to the alloys so deposited. More particularly, the process is directed to the electroplating of lead-tin alloys, predominantly lead, possessing certain desired physical properties as well as controlled composition.

It is an object of this invention to electroplate lead-tin alloys of homogeneous, dense, non-porous structure with a smooth, clean surface free from smut, films, nodules, trees, or spongy type of surface.

Another object of this invention is to control the ratio of the co-deposited metals, lead and tin, with respect to the ratio of concentration of these metals in the plating bath.

Another object is to deposit lead-tin alloys of desired physical properties and composition at high current densities and high efficiencies over a relatively wide range of operating conditions.

These and other features, objects and advantages of this invention, which will become apparent from a disclosure thereof, are simultaneously accomplished by the use of specially compounded organic addition agents in acid fluoborate plating baths for plating lead-tin alloys of desired composition and properties.

The co-deposition of lead and tin from acid fluoborate and sulfamate baths has been proposed. Without the use of organic addition agents in such baths it is necessary to have a much higher tin-lead ratio in the bath than obtained in the deposit therefrom when such deposits are predominantly lead. For example, to obtain a deposit analyzing 90% lead and 10% tin, it is necessary to have these metals in the bath in nearly a 1:1 ratio. Moreover, under such conditions, a little change in the metal ratio in the bath results in a big change in deposit composition; hence it is difficult to maintain constant deposit and bath composition. Also, deposits from baths containing no organic addition agents are dark in color and the surface is covered with a loose film of spongy material that is very objectionable for most uses, particularly when such deposits have to be soldered. A surface film, objectionable from the standpoint of soldering, especially with high speed machines, was also found on all lead-tin alloy deposits obtained from fluoborate and sulfamate baths containing addition agents disclosed in the prior art.

In the literature, glue or gelatin has been suggested as a desirable addition agent to acid fluoborate or sulfamate electrolytes for the deposition of lead-tin alloys. U. S. Patent 2,460,252 advocates the use of several organic addition agents, with or without glue, in fluoborate or sulfamate electrolytes for the deposition of lead-tin alloys containing around 5% of tin, from solutions containing 5 parts of tin or less per 100 parts of lead by weight. The virtue claimed for these addition agents and their combination is that they cause preferential deposition of tin, thus permitting the use of lower concentrations of tin in the plating bath than would otherwise be possible, in order to secure around 5% of tin in the deposit. However, none of the organic addition agents disclosed in this patent or in the electroplating literature on the subject is satisfactory from the standpoint of the physical characteristics of lead-tin alloy deposits, particularly with respect to high speed machine solderability and freedom from porosity.

Lead-tin alloys containing around 10–20% of tin have been found to be especially valuable as coatings for thin strip steel to be used in the manufacture of containers. Such coatings are not only protective against corrosion, but make possible easy high speed machine soldering of the overlapping joints formed in the manufacture of such containers. Heretofore such coatings have been applied to strip steel by passing it through a molten alloy bath, but such "hot-dipped" coatings as they are called, are not satisfactory from the soldering standpoint, particularly machine solderability, as they are too thin if wiped and too thick if not. It is not commercially feasible to apply hot-dipped lead-tin coatings much over 0.00002 inch thick on strip steel if the molten coating is wiped before cooling, while if this step is omitted, the coating is much too heavy economically. By the process of electrodeposition, however, alloy coatings of any desired thickness may be applied, but such coatings applied from baths available prior to my invention are covered by a film which interferes with the high speed machine soldering operation, especially when such films are oiled, as is common practice in the art. It has been found that electroplated lead-tin alloy coatings around 0.00005 to 0.0001 inch thick provide adequate protection and solder easily in the high speed machines, provided the electrodeposited alloy is dense, smooth, homogeneous, essentially non-porous and free from smut film.

In order to apply lead-tin alloy coatings containing about 10–20% tin on strip steel economically, it is necessary to plate the strip continuously at relatively high current densities. It is also economically desirable to use a plating bath with as low a tin content as possible to cut down on dragout losses. It is also desirable to have a plating bath composition that will deposit a relatively constantly proportioned deposit over the ranges of operating conditions found to be economical commercially. Above all, it is essential to deposit a dense, homogeneous, non-porous coating with a clean, smooth surface, free from loose films, smut, nodules, trees or anything that will interfere with the soldering operation, particularly when done mechanically with high speed soldering machines, as in the manufacture of containers.

In order to achieve the desired results and accomplish the objects of this invention it was found necessary to go beyond the disclosures of the prior art as none of them were sufficient to success. I have now found, however, that the desired results and objects can be obtained by the use of one of a class of specially compounded organic addition agents in an acid fluoborate electrolyte. The addition agents of this special class are made by reacting ethylene oxide with a phenol or a substituted phenol in which an organic radical is substituted for the hydroxyl hydrogen of a phenol. While such reaction products with the specific compounded phenol itself (C_6H_5OH) are effective, improved results are obtained by using multiple-ring phenols of higher molecular weight such as beta-naphthol for example, or substituted phenols such as diphenyl ether. When ethylene oxide is reacted with beta naphthol or diphenyl ether, condensation is believed to take place and the reaction product is considered a condensation product. Diphenyl ether is the name commonly given to a compound represented by two phenyl groups joined through an oxygen atom in the conven-

tional ether linkage. However, this compound may also be considered as a substituted phenol, in which the hydroxyl hydrogen of phenol is substituted by a phenyl group. It is so considered for the purposes of classification herein.

In general, as addition agents, I prefer reaction products containing 10–20 molecules of ethylene oxide per molecule of a phenol or a substituted phenol, although I do not wish to be limited by these ratios, since compounds containing none or less ethylene oxide are effective. These proportions are to be understood as reciting a generally preferred range. For example, I have found reaction products containing ethylene oxide and beta-naphthol in the proportion of approximately 10–15 molecules of ethylene oxide to one molecule of beta-naphthol to be particularly satisfactory. For convenience, this addition agent will be hereinafter referred to as an ethylene oxide-beta naphthol reaction product. In view of the new and unexpected results obtained by the use of this product, it is interesting to note that U. S. Pat. 2,460,252, referred to before, discloses naphthol as an addition agent in a lead-tin fluoborate bath but states that it produces a "powdery deposit not suitable for use as a protective coating."

The electroplating bath formulation and operating conditions that I have found particularly suitable for the deposition of lead-tin alloys containing about 10% tin on thin strip steel in a continuous strip plating operation are shown in Example I.

EXAMPLE 1

Lead fluoborate to make lead content.	95–105 grams per liter.
Stannous fluoborate to make stannous tin content equal.	12–14 grams per liter.
Fluoboric acid (100%)	About 40 grams per liter.
Boric acid (optional)	About 25 grams per liter.
Addition agent: Ethylene oxide-beta naphthol reaction product.	About 1.5 grams per liter.
Temperature, preferred	90–100° F.
Cathode current density	About 60 A/SF.
Anode current density	About 60 A/SF.
Anodes, approximately	90% lead+10% tin.

While in the above example some values have been expressed as a range, it is not to be understood that in any way they represent limits, but rather that the values are approximate. Example I reflects actual commercial plant operating data. It is of course possible to vary the concentrations of the bath ingredients, bath temperature and the current densities over wide ranges, provided they are properly balanced. For example, it is not advisable to go much below around 75 to 100 grams per liter of lead as a base point, because more dilute baths, while operable, are not as suitable for high current density operation, which is economically desirable, and are inclined to be more critical to control in order to maintain deposit composition reasonably constant. On the other hand, it is of course possible to increase bath concentration considerably, but there is little to be gained thereby from an operating standpoint, and dragout losses increase in proportion to the bath concentration.

The amount of fluoboric acid used is not critical, so long as there is sufficient free acid present to promote adequate anode corrosion, or in other words, to result in 100% anode current efficiency without polarization at operating current densities. The relationship between fluoboric acid concentration and anode current density shown in Example I has been found to be satisfactory for commercial operation.

Likewise the boric acid concentration is not at all critical; in fact it is not necessary to add boric acid if the lead and tin fluoborates and the fluoboric acid used in making the bath contain no free hydrofluoric acid. The principal function of the boric acid is to insure the absence of free hydrofluoric acid in the plating bath as it has been found that better results are generally assured under such conditions, although acceptable results can be obtained without adding boric acid. An appreciable concentration of boric acid, such as recommended in Example I has been found to promote uniformity of results under a variety of operating conditions.

The addition agent concentration is not critical above about one gram per liter, so it is an advantage to keep somewhat above that value. The addition agent is not consumed appreciably by the electrolysis, but is of course lost in dragout, and must be added as required. Need for more addition agent can be detected by a falling off in tin content and deterioration in the appearance of the deposit, particularly by the formation of a dark film or scum or smut on the surface. It is good operating practice to run periodic laboratory plating tests on small portions of the bath mixed with equal portions of fresh electrolyte of the same compositions containing no addition agent. This procedure effectively cuts the addition agent concentration in half for test purposes. If test plates from such a mixture are satisfactory there is of course plenty of addition agent in the bath. If they are not, small increments of the addition agent should be added to the test cell until a satisfactory plate is obtained. From the amount added to the test cell it is simple to calculate the amount needed in the commercial bath to assure continued good operation.

The composition of the anodes should be essentially the same as the composition of the deposit desired, as they dissolve uniformly in the bath and maintain it relatively constant in composition.

As another example of an embodiment of my invention, I have found reaction products of ethylene oxide and diphenyl ether, containing 10–20 molecules of ethylene oxide to one molecule of diphenyl ether to be very good addition agents. The following bath composition and operating conditions were found commercially satisfactory for production of lead-tin alloy deposits analyzing around 20% tin:

EXAMPLE 2

Lead fluoborate to make lead content.	95–105 grams per liter.
Stannous fluoborate to make stannous tin content equal.	23–25 grams per liter.
Fluoboric acid (100%)	About 40 grams per liter.
Boric acid (optional)	About 25 grams per liter.
Addition agent: Ethylene oxide-diphenyl ether reaction product.	About 1.5 grams per liter.
Temperature, preferred	90–100° F.
Cathode current density	About 60 A/SF.
Anode current density	About 60 A/SF.
Anodes, approximately	80% lead+20% tin.

In general, the same remarks apply to Example 2 as to Example 1. It is apparent from Examples 1 and 2 that alloy deposits containing from 10 to 20% tin can be obtained by proportionately varying the bath between the figures shown in the examples. Either of the specific addition agents given in the examples may be used for either 10 or 20% tin alloy deposits. It is of course possible to produce by the process of this invention alloy deposits containing less than 10% tin and more than 20% tin by varying the stannous tin content of the bath proportionately, although as the tin content of the deposit decreases below about 10% it becomes increasingly difficult to maintain desirable physical properties, and somewhere around 5% the low practical limit is reached. On the other hand, as the tin content of the alloy deposit increases, the desirable physical properties are easier to maintain, but the cost increases, so the upper limit for tin content of lead-tin alloy deposits is governed mainly by economics.

The lead-tin alloy deposits obtained from the process of this invention are new and novel with respect to similar electrodeposits obtained from prior art processes in that they resemble cast metal in appearance and structure, being homogeneous, dense, non-porous and semi-lustrous, with a clean, smooth surface free from such undesirable conditions as loose powder or dark films, smut, scum, nodules, trees or any other irregularities associated with lead-tin electrodeposits from baths of the prior art containing the conventional addition agents. By reason of this exceptional surface condition, the surface remains

clean and uncontaminated during handling, storage and shipment, and can be soldered perfectly, particularly on high speed machines without pre-cleaning or brushing, or any other preparatory treatment. The clean surfaces, characteristic of the alloy deposits of my invention, can be oiled so as to facilitate container manufacturing procedures, and the oiled surfaces can readily be machine soldered, just as in the case of pure tin. On the other hand, surfaces of deposits produced from prior art baths, when so oiled, cannot be readily machine soldered, as the surface films characteristic of such deposits make a mush with the oil which interferes with rapid soldering on high speed machines.

The great superiority of lead-tin alloy deposits plated from baths containing my novel addition agent over deposits of the same composition plated from conventional prior art baths with respect to continuity or imperviousness of the plated coating or freedom from pores, or as this property is more commonly expressed, highly nonporous plate, has been demonstrated by comparative salt spray tests. Two sets of lead-tin alloy deposits containing 15% tin, balance lead, were plated on flat steel test panels measuring 3 inches by 6 inches by .024 inch from a bath containing my novel addition agent, and from a typical prior art bath containing resorcinol and glue as addition agents. Test panels were plated from each bath under identical conditions to produce deposits of four different thicknesses: .00005 inch, .0001 inch, .00015 inch, and .0002 inch, respectively. Three test panels were plated for each thickness from each bath, making a total of 24 test panels, which were then submitted to the standard A. S. T. M. salt spray test. The panels were removed at intervals and the rust spots on each panel were counted. The figures obtained for each set of three panels of the same thickness from each bath were averaged. The results are shown in Table I following, in which, for convenience, the letter A is used to identify the test panels plated in the bath containing my novel addition agent, and the letter B is used to identify the test panels plated in the bath containing resorcinol and glue as addition agents.

Table I

AVERAGE NUMBER OF RUST SPOTS

Cumulative Hours in Salt Spray	Thickness of Deposit							
	.00005 in.		.0001 in.		.00015 in.		.0002 in.	
	A	B	A	B	A	B	A	B
15	8	26	1	7	1	7	1	7
40	14	35	1	8	1	7	1	9
63	19	38	2	14	1	10	1	9
85	—	—	2	—	2	—	2	16
107	------	------	3	—	3	—	2	—

The dash, (—), in the above table indicates that rusting had progressed to the point where individual rust spots no longer could be counted.

Comparison of the figures in Table I clearly shows that the deposits from the bath containing my novel addition agent are much more impervious, or non-porous, than deposits from a typical prior art bath.

While the invention has been described as embodied in concrete form and as operating in a specific manner in accordance with the provisions of the patent statutes, it should be understood that the invention is not limited thereto, since various modifications will suggest themselves to those skilled in the art without departing from the spirit of the invention.

For example, the alloy plate of my invention may be applied to metals other than steel, such as aluminum, copper, brass, etc., in fact to any electrically conductive surface such as metallized plastic, all of which may be in sheet form or in the form of any discrete object.

What is claimed is:

1. An electrolyte for the electrodeposition of lead-tin alloys comprising an aqueous solution of lead fluoborate, tin fluoborate, fluoboric acid and approximately one to two grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide with beta naphthol.

2. An electrolyte for the electrodeposition of lead-tin alloys comprising an aqueous solution of lead fluoborate, tin fluoborate, fluoboric acid and approximately one to two grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide with beta naphthol combined in the proportions of approximately 10 to 15 molecules of ethylene oxide to one molecule of beta naphthol.

3. An aqueous lead-tin alloy electroplating bath comprising substantially approximately 100 grams per liter of lead as fluoborate, approximately 10–25 grams per liter of tin as stannous fluoborate, fluoboric acid, and approximately 1 to 2 grams of ethylene oxide-beta naphthol condensation product.

4. An aqueous lead-tin alloy plating bath consisting substantially of 95 to 105 grams per liter of lead as fluoborate, 12–14 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, boric acid and approximately 1.5 grams per liter of ethylene oxide-beta naphthol condensation product.

5. An aqueous lead-tin alloy plating bath consisting substantially of 95–105 grams per liter of lead as fluoborate, 23–25 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, boric acid and approximately 1.5 grams per liter of ethylene oxide-beta naphthol condensation product.

6. An aqueous lead-tin alloy plating bath comprising fluoboric acid, lead as fluoborate in concentration above about 75 grams of lead per liter, tin as stannous fluoborate in concentration of approximately ⅛ the concentration of lead by weight to each 10% of tin desired in the deposit, and an addition agent of ethylene oxide-beta naphthol condensation product in concentration of over about one gram per liter.

7. The method of producing a homogeneous, dense, nonporous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the surface as a cathode and an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating in an aqueous fluoboric acid electrolyte, and depositing a lead tin alloy from said aqueous electrolyte containing fluoborates of lead and tin and containing approximately one to two grams per liter of a bath-soluble addition agent composed of ethylene oxide-beta naphthol condensation product.

8. As an article of manufacture a solderable coated product comprising a base metal having thereon a coating of an alloy of lead and tin containing between 10% and 20% tin, said coating being homogeneous, dense, non-porous and semi-lustrous with a clean, smooth surface free from irregularities and applied by the process of claim 7.

9. The method of producing a homogenous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the surface as a cathode, in an aqueous acidic electrolyte containing fluoboric acid and fluoborates of lead and tin and containing approximately one to two grams per liter of a bath-soluble addition agent composed of ethylene oxide condensed with beta naphthol in the proportion of approximately 10 to 15 molecules of ethylene oxide to one molecule of beta naphthol, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and

passing an electric current through the electrolyte, thereby depositing a lead-tin alloy coating therefrom.

10. In the process of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metalic strip, the steps comprising passing the strip as a cathode through an aqueous electrolyte consisting substantially of aprpoximately 100 grams per liter of lead as lead fluoborate, approximately 10–25 grams per liter of tin as stannous fluoborate, fluoboric acid and approximately 1 to 2 grams per liter of ethylene oxide-beta naphthol condensation product in which the constituents are combined in the proportion of approximately 10 to 15 molecules of thylene oxide to one molecule of beta naphthol, and passing an electric current through the electrolyte and the said cathode strip, thereby depositing a coating on the strip from the electrolyte.

11. The method of producing a homogeneous, dense, nonporous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metallic strip which comprises the steps of immersing the strip as a cathode, in an aqueous electrolyte consisting substantially of 95 to 105 grams per liter of lead as lead fluoborate, 12–14 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, approximately 25 grams per liter of boric acid and approximately 1.5 grams per liter of ethylene oxide-beta naphthol condensation product, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and passing an electric current through the electrolyte, thereby depositing a lead tin alloy coating therefrom.

12. The method of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metallic strip which comprises the steps of immersing the strip as a cathode in an aqueous electrolyte consisting substantially of 95–105 grams per liter of lead as lead fluoborate, 23–25 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, approximately 25 grams per liter of boric acid and approximately 1.5 grams per liter of ethylene oxide-beta naphthol condensation product, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and passing an electric current through the electrolyte, thereby depositing a lead-tin alloy coating therefrom.

13. The method of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the strip as a cathode, in an aqueous electrolyte comprising substantially fluoborate acid, lead as fluoborate in concentration above about 75 grams of lead per liter, tin as stannous fluoborate in concentration of approximately one-eighth the concentration of lead by weight to each 10% of tin desired in the deposit and an addition agent of ethylene oxide-betanaphthol condensation product in concentration of over about one gram per liter, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and passing an electric current through the electrolyte, thereby depositing a lead tin alloy therefrom.

14. In a process for electroplating a lead-tin alloy from an acid fluoborate electrolyte comprising an aqueous solution of lead fluoborate, tin fluoborate and fluoboric acid, the steps of regulating the composition of the deposit, providing a homogeneous, dense, non-porous and semi-lustrous coating, and avoiding the formation of smut on the surface, by maintaining in the electrolyte a condensation product of ethylene oxide and beta naphthol at a concentration of approximately one to two grams per liter.

15. An electrolyte for the electrodeposition of lead-tin alloys comprising an aqueous solution of lead fluoborate, tin fluoborate, fluoboric acid and approximately one to two grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide with a material from the group consisting of beta-naphthol and diphenyl ether.

16. An electrolyte for the electrodeposition of lead-tin alloys comprising an aqueous solution of lead fluoborate, tin fluoborate, fluoboric acid and approximately one to two grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide with diphenyl ether.

17. A method of producing a homogeneous, dense, nonporous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the surface as a cathode and an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating in an aqueous fluoboric acid electrolyte, and depositing a lead tin alloy from said aqueous electrolyte containing fluoborates of lead and tin and containing approximately one to two grams per liter of a bath-soluble agent composed of a condensation product of ethylene oxide with a material from the group consisting of beta naphthol and diphenyl ether.

18. A method of producing a homogeneous, dense, nonporous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the surface as a cathode and an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating in an aqueous fluoboric acid electrolyte, and depositing a lead tin alloy from said aqueous electrolyte containing fluoborates of lead and tin and containing approximately one to two grams per liter of a soluble agent composed of a condensation product of ethylene oxide and diphenyl ether.

19. As an article of manufacture, a solderable coated product comprising a base metal having thereon a coating of lead and tin containing between 10% and 20% tin, which coating is homogeneous, dense, non-porous, semi-lustrous, and with a clean smooth surface free from irregularities and applied by the process of claim 18.

20. An aqueous lead-tin alloy electroplating bath comprising substantially approximately 100 grams per liter of lead as lead fluoborate, approximately 10–25 grams per liter of tin as stannous fluoborate, fluoboric acid, and approximately 1 to 2 grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide and diphenyl ether.

21. An aqueous lead-tin alloy plating bath consisting substantially of 95 to 105 grams per liter of lead as lead fluoborate, 12–14 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, boric acid and approximately 1.5 grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide and diphenyl ether.

22. An aqueous lead-tin alloy plating bath consisting substantially of 95–105 grams per liter of lead as lead fluoborate, 23–25 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, boric acid and approximately 1.5 grams of addition agent per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide and diphenyl ether.

23. An aqueous lead-tin alloy plating bath comprising fluoboric acid, lead as fluoborate in concentration above about 75 grams of lead per liter, tin as stannous fluoborate in concentration of approximately ⅛ the concentration of lead by weight to each 10% of tin desired in the deposit, and an addition agent in concentration of over about one gram per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide and diphenyl ether.

24. The method of producing a homogeneous, dense,

non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the surface as a cathode, in an aqueous acidic electrolyte containing fluoboric acid and fluoborates of lead and tin and containing approximately one to two grams of addition agent per liter of electrolyte, said addition agent consisting of ethylene oxide condensed with a diphenyl ether in proportions of approximately 10 to 25 molecules of ethylene oxide to 1 molecule of diphenyl ether.

25. In the process of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metallic strip, the steps comprising passing the strip as a cathode through an aqueous electrolyte consisting substantially of approximately 100 grams per liter of lead as lead fluoborate, approximately 10–25 grams per liter of tin as stannous fluoborate, fluoboric acid and approximately 1 to 2 grams per liter of addition agent consisting of ethylene oxide condensed with diphenyl ether in which the constituents are combined in the proportions of approximately 10 to 15 molecules of ethylene oxide to one molecule of diphenyl ether, and passing an electric current through the electrolyte and the said cathode strip, thereby depositing a coating on the strip from the electrolyte.

26. The method of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metallic strip which comprises steps of immersing the strip as a cathode, in an aqueous electrolyte consisting substantially of 95 to 105 grams per liter of lead as lead fluoborate, 12–14 grams per liter of tin as stannous fluoborate, approximately 40 grams per liter of fluoboric acid, approximately 25 grams per liter of boric acid and approximately 1.5 grams per liter of addition agent consisting of condensation product of ethylene oxide and diphenyl ether, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and passing an electric current through the electrolyte, thereby depositing a lead tin alloy coating therefrom.

27. The method of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon a metallic strip which comprises the steps of immersing the strip as a cathode in an aqueous electrolyte consisting substantially of 95–105 grams per liter of lead as lead fluoborate, 23–25 grams per liter of tin as stannous fluoborate, approximately 25 grams per liter of boric acid and approximately 1.5 grams per liter of addition agent consisting of a condensation product of ethylene oxide and diphenyl ether, immersing in said electrolyte an anode composed of lead-tin alloy having about the proportions of lead and tin desired in the plating and passing an electric current through the electrolyte, thereby depositing a lead-tin alloy coating therefrom.

28. The method of producing a homogeneous, dense, non-porous, semi-lustrous, smooth-surfaced plating of an alloy of lead and tin upon an electrically conducting surface which comprises the steps of immersing the strip as a cathode, in an aqueous electrolyte comprising substantially fluoboric acid, lead as fluoborate in concentration above about 75 grams of lead per liter, tin as stannous fluoborate in concentration of approximately one-eighth the concentration of lead by weight to each 10% of tin desired in the deposit, and an addition agent in concentration of over about one gram per liter of electrolyte, said addition agent consisting of a condensation product of ethylene oxide and diphenyl ether.

29. In a process for electroplating a lead-tin alloy from an acid fluoborate electrolyte comprising an aqueous solution of lead fluoborate, tin fluoborate, and fluoboric acid, the steps of regulating the composition of the deposit, providing a homogeneous, dense, non-porous and semi-lustrous coating, and avoiding the formation of smut on the surface, by maintaining in the electrolyte a condensation product of ethylene oxide and diphenyl ether in concentration of approximately 1 to 2 grams per liter.

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