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Beckwith et al.

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[54] **BATH AND METHOD FOR ELECTRODEPOSITING TIN AND/OR LEAD**

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

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[57] **ABSTRACT**

A plating bath for electrodepositing tin and/or lead contains stannous ion, lead ion, or a mixture thereof, together with a fluoborate, fluosilicate and/or sulfamate electrolyte and a polyoxyalkylated fatty acid alkylolamide surfactant. The bath operates at pH values of less than about 3.0, and very desirable deposits are produced over wide ranges of current densities and under a variety of plating conditions.

36 Claims, No Drawings

BATH AND METHOD FOR ELECTRODEPOSITING TIN AND/OR LEAD

BACKGROUND OF THE INVENTION

As is well known, electrodeposits of tin and/or lead are employed in a wide variety of decorative and functional applications. Notwithstanding the availability of different types of formulations for the production of such deposits, there has remained a need for a bath having an optimum combination of characteristics. In many instances the electrodeposits produced from the presently available baths are deficient in one or more desired physical characteristics such as smoothness, uniformity, fine grain structure, and freedom from porosity; frequently the baths produce satisfactory results only under limited conditions of operation which are often not entirely practical or economically desirable.

Recently there has been developed a highly satisfactory bath for the electrodeposition of tin/lead alloys which is described and claimed in copending United States Application for Letters Patent of Grace F. Hsu, Ser. No. 83,229, filed on Oct. 22, 1970, and assigned to the assignee of the present invention. In the course of the developmental activity with respect to the aforementioned invention it was found that tin and lead alone, or in combination, could be plated advantageously and efficiently from a novel bath. It was also found that the conditions of operation and composition could be varied depending upon the metal being electrodeposited and the characteristics desired in the metal deposit.

Accordingly, it is an object of the present invention to provide a novel electroplating bath which is capable of producing highly desirable deposits of tin, lead and alloys thereof.

It is also an object of the invention to provide such a bath which is capable of producing a deposit that is smooth, substantially free of porosity, uniform, relatively fine in grain structure and/or bright when so desired, and which may also be of an optimum composition for soldering in the case of the alloy compositions.

Another object is to provide such a bath which operates with good efficiency and over a broad range of current density.

Still another object of the invention is to provide a novel electroplating method for the production of a high quality tin, lead or tin/lead alloy deposit, which method is rapid, efficient, and effective, and which may be conducted under convenient and practical conditions over a broad range of current density.

A further object is to provide a high speed electroplating method for tin, lead and alloys thereof based upon the novel bath and particularly advantageous for wire plating operations.

SUMMARY OF THE DISCLOSURE

It has now been found that the foregoing and related objects can be readily attained in an aqueous acid plating bath comprising about 15.0 to 350.0 grams per liter of an ion selected from the group consisting of stannous ion, lead ion, and mixtures thereof, and about 100.0 to 500.0 grams per liter of a radical selected from the group consisting of a fluoborate, fluosilicate, sulfamate, and mixtures thereof. The bath contains about 5.0 to 50.0 grams per liter of an alkoxylated fatty acid alkylolamide surfactant, and it has a pH less than about 3.0.

Preferably, the alkylolamide surfactant is present in an amount of about 10.0 to 25.0 grams per liter, the bath has a pH of about 0.1 to 1.5, and the electrolyte radical is fluoborate. The bath may also contain, in addition to the foregoing components, about 0.1 to 10.0, and preferably about 0.3 to 2.0 grams per liter, of a ring halogenated aromatic aldehyde which may be selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde; about 2.0 to 15.0 grams per liter of an aromatic amine which may be selected from the group consisting of toluidines and aniline; about 0.5 to 3.0 grams per liter of a trichlorinated benzene derivative which is most desirably 1,2,4-trichlorobenzene; and/or about 2.0 to 25.0 grams per liter of a lower aliphatic aldehyde containing one to four carbon atoms, which is most desirably formaldehyde. The bath may also include, in combination with an aromatic amine, about 0.1 to 10.0 grams per liter of a carbonyl-containing compound selected from the group consisting of benzylidene acetone, 3-hydroxybutanal, thiophenealdehyde, benzaldehyde, 2,5-dimethoxybenzaldehyde, tolualdehyde, cinnamaldehyde, and anisaldehyde.

For the production of optimum lead deposits the bath, generally comprised as hereinbefore set forth, will contain at least about 75.0 grams per liter of lead ion and will be substantially free of tin ions. Preferably, such a lead bath will contain at least about 150.0 grams per liter of lead ion, and will additionally contain about 0.5 to 5.0 grams per liter of a polyethoxylated alkyl phenol secondary surfactant.

When employed for the production of a tin deposit, the bath will be substantially free of lead ion and will contain at least about 75.0 grams per liter of stannous in. Preferably, such a bath will contain about 100.0 to 150.0 grams per liter of the stannous ion, and it may advantageously include about 0.5 to 3.0 grams per liter of a trichlorinated benzene derivative.

To produce tin/lead alloy deposits in which the amount of tin advantageously predominates, the concentration of stannous ion in the bath will be about 10.0 to 180.0 grams per liter, and that of the lead ion will be about 90.0 to 6.0 grams per liter. Preferably, the electrolyte in such a bath is provided by at least about 150.0 grams per liter of the fluoborate radical, with the bath containing at least about 50.0 grams per liter of free fluoboric acid and free boric acid from at least about 10.0 grams per liter to saturation. The bath may desirably contain an aromatic aldehyde or a trichlorinated benzene derivative as set forth above, and most desirably these components are present in combination. It may, in addition, contain an aromatic amine and/or formaldehyde; when the aromatic amine is present, a carbonyl-containing compound of the group hereinbefore identified may also be included. It is especially desirable that the amount of the stannous ion in such an alloy bath be about 45.0 to 65.0 grams per liter and that the amount of lead ion therein be about 30.0 to 20.0 grams per liter.

The bath may also be optimally composed to produce tin/lead alloy deposits wherein the amount of lead advantageously predominates, in which instance it should contain about 10.0 to 30.0 (most desirably about 15.0 to 20.0) grams per liter of stannous ion and about 200.0 to 100.0 (most desirably about 175.0 to 150.0) grams per liter of the lead ion. For especially desirable results, the bath will contain about 0.5 to 5.0 grams per

liter of a polyethoxylated alkylphenol secondary surfactant.

Highly desirable metal deposits are readily attained under economically advantageous conditions in an electroplating method wherein the aqueous acid plating bath, comprised as has hereinbefore been described, is prepared and maintained at a temperature of about 50° to 150° Fahrenheit. A workpiece having a metallic surface, and at least one anode of a metal selected from the class consisting of tin, lead, and alloys thereof, are immersed in the bath, and a voltage is applied thereacross to provide a current density of about 2.0 to 2,000.0 amperes per square foot at the workpiece, thereby depositing the metal upon the metallic surface; preferably, the bath and/or the workpiece is agitated.

In instances in which the bath contains at least 150.0 grams per liter of lead ion and is substantially free from tin ions, or in which it contains about 45.0 to 65.0 grams per liter of stannous ion and about 30.0 to 20.0 grams per liter of lead ion, the current density at the workpiece may preferably be less than about 100.0 amperes per square foot. When the bath contains about 100.0 to 150.0 grams per liter of stannous ion and is substantially free from lead ion, or when it contains about 15.0 to 20.0 grams per liter of stannous ion and about 175.0 to 150.0 grams per liter of lead ion, the current density may preferably be greater than about 400.0 amperes per square foot, and most desirably it is at least about 600.0 amperes per square foot; the workpiece and the bath may be moved relative to one another at a rate of at least about 150.0 lineal feet per minute to provide a high speed plating method. The various additives and combinations thereof hereinbefore set forth may be included in the baths used in the practice of the novel method of the invention, and in most cases the pH of the bath employed will preferably be about 0.1 to 1.5.

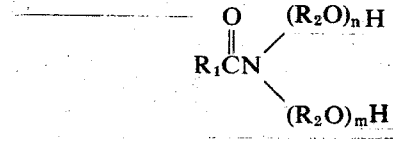
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be appreciated, the amounts of the tin and/or lead ions present in the bath will depend upon a number of factors, primary considerations being the desired composition of the electrodeposited metal and, to lesser degrees, the technique employed, the conditions of the operation, etc. In any event, to obtain satisfactory results the concentration of the cation to be electrodeposited (be it tin, lead, or a mixture thereof) must be from about 15.0 to 350.0 grams per liter because amounts outside of the range will result in poor efficiency, sludging, precipitation, etc., and will tend to produce deposits of unacceptable quality. When either the tin ion or the lead ion is employed in the substantial absence of the other, it is preferred that the concentration of the cation be at least about 75.0 grams per liter; most desirably, when lead is employed alone it will be present in an amount of at least 150.0 grams per liter and, when tin is the only cation present, its concentration should be in the range of about 100.0 to 150.0 grams per liter.

When the bath is utilized for the production of a tin/lead alloy deposit wherein tin predominates, the concentrations of tin and lead will generally be about 10.0 to 180.0 and about 90.0 to 6.0 grams per liter, respectively; most desirably, such a bath will contain about 45.0 to 65.0 grams per liter of the stannous ion and about 30.0 to 20.0 grams per liter of the lead ion. On the other hand, when the alloy deposit is to contain a predominant amount of lead, the bath may advantageously contain about 10.0 to 30.0 grams per liter of stannous ion and about 200.0 to 100.0 grams per liter of lead ion; preferably, the concentrations of the respective metals in such a bath will be about 15.0 to 20.0 and about 175.0 to 150.0 grams per liter. One desirable feature of the present invention is that it enables the formation of an electrodeposit having a composition at or near the eutectic point for tin/lead alloys. The most desirable ranges for the concentrations of the ions in such a bath are about 53.0 to 57.0 grams per liter of stannous ion and about 27.0 to 23.0 grams per liter of lead ion.

The electrolyte radical is fluoborate, fluosilicate, sulfamate, or mixtures thereof, although other noninterfering radicals may be present as the result of using salts to furnish all or a portion of the tin and lead ions with the desired radical. Thus, the electrolyte radicals may be provided as the acids or as salts of noninterfering cations. It should be appreciated that the terms "fluoborate," "fluosilicate," and "sulfamate" are used generically herein and encompass the more complex salts thereof, such as the phenolsulfamate compounds. Fluoborate electrolytes are preferred and, to be satisfactory, the bath should contain about 100.0 to 500.0 grams per liter of the fluoborate radical; preferably, the amount of the radical will be not less than about 150.0 grams per liter. Typically, such a bath will contain at least about 50.0 grams per liter of free fluoboric acid and at least about 10.0 grams per liter of free boric acid, although these quantities may vary considerably to obtain optimum results in specific baths. In many cases the bath will desirably be maintained at saturation with boric acid, and this condition can be assured simply by suspending a porous bag of boric acid in the solution.

The third essential component of the baths is a polyoxyalkylated fatty acid alkylolamide surfactant, which must be present in an amount of about 5.0 to 50.0 grams per liter, and preferably in an amount of about 10.0 to 25.0 grams per liter; at concentrations lower than about 10.0 grams per liter there is some tendency for the deposit to darken and to become porous, whereas more than about 25.0 grams per liter of the surfactant tends to cause coarseness. Alkylolamide surfactants that are suitable for use herein may have the following structural formula:



where R_1 is a fatty acid alkyl group, containing eight to 22 carbon atoms, R_2 is selected from the group consisting of ethylene, propylene, and mixtures thereof, m is an integer from zero to 15, n is an integer from one to 30, and the sum of m plus n is an integer from two to 30; generally, when m is other than zero it will be equal to n. Commercial products which may be employed to furnish the alkylolamide surfactant include the fatty acid derivatives sold by Stepan Chemical Company of Northfield, Ill. under the trademark AMIDOX. Specifically, the products designated by Stepan as AMIDOX C–2, C–5, L–2, and L–5 have been found to be particu-

larly beneficial, and that designated AMIDOX C–5 is preferred. It is believed that the AMIDOX products of the C series are ethoxylated coconut fatty acid monoethanolamides, and that the members of the L series are ethylene oxide condensates of lauric monoethanolamide. The associated numbers are believed to indicate the number of moles of ethylene oxide that have been used per mole of amide in producing the product. A second manufacturer of products that may be appropriate to provide this component of the baths is Armour Industrial Chemical Company of Chicago, Ill., which sells them under the trademark ETHOMID. Specific products are designated ETHOMID HT/15, HT/60 and O/15, wherein the designation HT and O indicate that the product is either a hydrogenated-tallow amide or an oleamide derivative, respectively; subtraction of 10 from the associated numeral indicates that the number of moles of ethylene oxide that are believed to be present in a molecule of the compound. It should be appreciated that, in some instances, best results may be achieved when a combination of two or more of the foregoing alkylolamide surfactants is utilized.

In some of the baths falling within the scope of the present invention, a secondary surfactant may be utilized in combination with the fatty acid alkylolamide derivative to produce optimum properties in the deposit. Exemplary of such secondary surfactants are polyalkoxylated alkylphenols, and especially the condensates of alkylphenols having six to 12 carbon atoms in the alkyl chain with an alkylene oxide selected from the class consisting of ethylene oxide, propylene oxide and mixtures thereof. Generally, these products will contain about five to 30 alkylene oxide groups in each molecule. Specific commercial products that may be advantageously employed are those sold by Atlas Chemical Industries, Inc. of Wilmington, Del. under the designations RENEX 650 and RENEX 697; the product sold by General Aniline and Film Corporation of New York, N.Y. under the designation IGEPAL CO–710; and the products designated NEUTRONYX 640, 656 and 675, which are sold by Onyx Chemical Company of Jersey City, N.J. The amount of the secondary surfactant employed will generally be in the range of about 0.5 to 5.0 grams per liter, and normally about 1.5 grams per liter thereof will be most satisfactory. Mixtures of different types of secondary surfactants may also be used, and specific alternative surfactants will be apparent to those skilled in the art in view of the foregoing disclosure.

In most instances, the baths will contain one or more carbonyl containing compounds to increase the level of brightness of the deposit. It is possible to employ any of a variety of different types of compounds for this purpose, such as the ring halogenated benzaldehydes, benzylidene actone, 3-hydroxybutanal, thiophene aldehyde, benzaldehyde, 2,5-dimethoxybenzaldehyde, tolualdehyde, cinnamaldehyde, anisaldehyde, etc. The ring halogenated benzaldehydes are preferred and particularly desirable results have been obtained using either 2,4-dichlorobenzaldehyde, or 2,6-dichlorobenzaldehyde. It has been found that the presence of about 2.0 to 15.0, and preferably about 3.0 to 8.0 grams per liter of a primary or secondary aromatic amine (such as ortho-toluidine, meta-toluidine, N-ethyl-ortho-toluidine, aniline, etc.) is highly desirable to obtain optimum results in the baths of the present invention using other than the ring halogenated benzaldehydes, whereas the ring halogenated benzaldehydes can produce comparable deposits in the absence of such amines. Although the specific amount will depend upon the particular carbonyl compound involved, the minimum effective concentration of these compounds will generally be at least about 0.1 gram per liter; usually, at least about 0.3 gram per liter thereof will yield desirable results. More than about 10.0 grams per liter will, in most cases, be without additional benefit; the preferred upper limit is about 2.0 grams per liter from the standpoint of economy and minimizing unnecessary concentrations of components.

When the bath contains a carbonyl compound or other brightening agent, it will usually be desirable to also include at least about 2.0 to 25.0 grams per liter of a lower aliphatic aldehyde (i.e., one containing one to four carbon atoms). The presence of this additive appears to widen the range of current density over which a bright deposit is obtained and to otherwise improve operation (such as making the bath less sensitive to variations); formaldehyde is preferred. An additional additive that is very beneficially included in the bath is a trichlorinated benzene derivative, and most often 1,2,4-trichlorobenzene will be employed. Its use in an amount of about 0.5 to 3.0 grams per liter tends to increase brightness at the lower end of the current density range and to smooth the deposit and reduce or eliminate the so-called "orange peel" effect which may otherwise occur.

Among the other additives which may be included to modify the operation of the present bath are auxiliary surfactants, secondary brighteners, and other materials, such as the polyvinyl alcohols, peptone, resorcinol, glue, gelatine, beta-naphtol, etc. When used, these additives should usually be included in amounts of about 0.5 to 7.5 grams per liter, and it has been found that about 0.5 to 5.0 grams per liter of cresylic acid may also be somewhat desirable. Although little or no tendency for metal sludge or precipitate formation has been noted in baths properly prepared and operated in accordance with the invention, in some instances it may be desirable to incorporate a chelating agent wuch as a citric acid, malic acid, or the aminopolyacetic acids (e.g., ethylenediamine tetraacetic acid, ethylenetriamine pentaacetic acid, nitrilotriacetic acid). Such chelating agents, when employed, are generally included in an amount of about 5.0 to 20.0 grams per liter.

Since some of the suitable brighteners and other components which may desirably be included in the bath exhibit relatively low solubility therein, it may be necessary or desirable to employ a solvent solution thereof to facilitate formulation of the bath. Among the various solvents that may be employed, depending upon the particular component involved, are the low molecular weight alcohols (methanol, ethanol, and propanol) and the low molecular weight glycol ethers (ethylene glycol monoethyl ether, etc.). Generally, the component will be added as a 0.1 to 5.0 and preferably as a 0.5 to 2.0 percent by weight solution so as to obtain a stable solvent solution which may be readily dispersed in the acid bath. In some instances, it may be most convenient to provide the majority or all of the bath components as a premixed solvent or concentrate solution, in which event the concentration of inert solvent (other than water) in the ultimate bath may be quite high.

Formulations falling within the scope of the present invention may be employed in rack, barrel, and wire plating operations, and accordingly the conditions under which they will be used may vary considerably. Thus, depending upon the type of plating operation and other factors such as temperature, agitation, etc., the current density may vary from about 2.0 to 2,000.0 amperes per square foot (ASF). In rack and barrel plating operations, the average current density will not generally exceed about 100.0 ASF, and will preferably be about 5.0 to 50.0 ASF; for wire plating operations the current density will not usually be less than about 400.0 ASF, and for bright deposits it will generally exceed about 600.0 ASF. With baths intended for the production of alloy deposits having a substantially eutectic composition, a narrow current density range of about 25.0 to 35.0 ASF has been found to be most desirable.

Although it is desirable in most instances to agitate the workpiece and/or the bath to obtain high quality uniform deposits and to avoid the development of sludge or film, particularly under conditions of high current density and/or temperature, agitation is not essential. Of course, in wire plating operations the workpiece and bath move rapidly relative to one another and the novel composition of the instant invention may be formulated to operate at wire speeds in excess of about 150, and preferably above 200, lineal feet per minute.

The plating efficiency of the bath is generally high, and in the optimum case will range up to about 95 percent, and above, based upon the theoretical rate of deposition. The applied voltage should be about 0.2 to 10.0 volts, and preferably plating will be carried out at about 0.5 to 5.0 volts; once again, the most desirable voltage level will depend upon the plating technique and conditions employed.

The baths should be operated at a temperature of about 50° to 150°, and preferably from about 60° to 90°, Fahrenheit; temperatures above about 80° Fahrenheit are often most desirable. Operation below about 50° Fahrenheit tends to be inefficient and to produce undesirable deposits, whereas temperatures higher than about 90° Fahrenheit may tend to cause oxidation of the tin ion (in the tin and tin/lead baths) to the stannic state and to produce somewhat dull and rough deposits; low temperatures are also preferred because of a tendency for the bath to be consumed at an excessive rate at temperatures that are unduly high. The pH should be less than 3.0, and preferably it will be 1.5 or below; generally, a pH of about 0.1 will represent the practical lower end of the range.

Any metallic substrate or metal-surfaced article which can be plated with tin or lead using prior art baths may generally be coated in accordance with the present invention. For example, good deposits may be produced upon articles of copper, nickel, iron, steel, etc. The best results are obtainable with these baths if relatively pure anodes of the respective metals are employed, and to produce tin/lead deposits either alloy anodes or separate tin and lead anodes may be used. It should be noted that the composition of the anode has a significant effect upon the composition of the alloy deposit, and that it is generally desirable to employ an anode having a proportion of metals approximating that desired in the plated deposit. The composition of the deposit may also be controlled by use of separate anodes of tin and lead, to which the current may be proportioned appropriately.

Filtration of the bath is not essential, but will normally be beneficial when contamination is encountered due to air-borne impurities and/or carryover from other finishing operations; preferably, it will be effected on a continuous basis. Various filtering media may be utilized including fabrics (such as of polypropylene) and other conventional filtering materials. The depletion of the various components of the bath is best corrected by analysis for the several components on a periodic basis which can be established for a given facility. To determine the amounts of stannous salt required, an iodine titration technique may be used; the lead content may be checked by precipitation with dilute surfuric acid. The amount of the surfactants and other components may be best evaluated by testing a sample of the bath in a suitable test cell, and a suitable schedule may be established for a given facility and workpiece.

As has previously been discussed, the baths of the present invention may be employed for the production of deposits containing either lead or tin, or to produce an alloy containing these elements in substantially any proportion, depending upon the characteristics desired in the ultimate product and the use for which it is intended. As has also been mentioned, tin/lead deposits having a composition at or near the eutectic value for the alloy (about 63/37) are optimum for soldering purposes and the present baths may be employed advantageously for the production thereof. Electro-deposits containing tin and lead in a 7:93 ratio, typically used for bearing contact surfaces, may also be produced with these formulations by proper selection of the bath components and the conditions of operation.

Depending upon the several variables hereinbefore discussed, the deposits produced in accordance herewith may vary from quite dull to specular brightness. They are generally very smooth and uniform in appearance, substantially free from porosity, and they tend to have relatively fine grain structures withou undesirable crystal growth (i.e., treeing). In addition, the deposits are fully adherent to the surface of the workpiece, and the bath composition may be such that even heavy deposits, i.e., those of about 1 to 4 mils in thickness, are free from peeling and cracking.

Illustrative of the efficacy of the present invention are the following specific examples, wherein all parts and percentages are on a weight basis unless specified to the contrary. Although the solutions employed are stable over long periods of use, a fresh solution is utilized in each of the Examples and no "working in" period is required.

EXAMPLE ONE

PART A

Into a 267 milliliter Hull cell is introduced an aqueous lead plating bath containing water and amounts of lead fluoborate, fluoboric acid, and boric acid sufficient to provide therein about 168.0 grams per liter of lead metal, about 15.0 grams per liter of free fluoboric acid, about 22.5 grams per liter of free boric acid and a pH less than about 1.5. Also included in the bath is about 15.0 grams per liter of a coconut fatty acid alkylolamide surfactant containing about 5 moles of ethylene oxide per mole thereof (sold by Stepan Chemical Company of Northfield, Illinois as AMIDOX C-5), and

about 1.5 grams per liter of an ethoxylated nonylphenol surfactant containing about 30 moles of ethyleneoxide per molecule thereof (sold by Atlas Chemical Industries of Wilmington, Delaware under the trademark RENEX 650). Into the cell is placed a clean steel panel and a lead anode, and plating is effected with a current of two amperes for 5 minutes at room temperature, without agitation. Over a wide current density range of about 2.0 to 100.0 amperes per square foot, a uniform lead deposit is produced which is light grey in color, exhibits a slight sheen, is fine in grain structure and is substantially free from undesirable crystal growth; it is found to be substantially non-porous and very adherent to the panel, the edge characteristics are good, and there is no evidence of cracking or peeling even at thicknesses of about 4 mils.

PART B

The bath described in Part A thereof is employed at temperatures of 80°, 90°, 100°, 110°, and 130° Fahrenheit, and at voltages of 3.5, 3.5, 3.0, 3.0, and 2.75 respectively. It is seen that the increase in temperature refines the grain structure of the deposit at current densities above about 50.0 ASF, and that the high temperatures do not significantly deteriorate the quality of the deposit obtained.

PART C

Part A of this example is repeated using the same bath, but omitting the secondary surfactant (i.e., the nonylphenol derivative) therefrom. Although some porosity is encountered at the extreme low end of the plating range, the deposit is of good quality and free from porosity at current densities of about 10.0 to 80.0 ASF. Substitution of the nonylphenol ethoxylated product sold by Atlas Chemical Industries under the trademark RENEX 697, and that sold by General Aniline and Film Corporation under the trademark IGEPAL CO-710 for the RENEX 650, is found to produce results that are substantially equivalent to those obtained in Part A.

EXAMPLE TWO

PART A

An aqueous bath is prepared by admixing with water sufficient quantities of stannous fluoborate and fluoboric acid to provide about 120.0 grams per liter of stannous ion and about 140.0 grams per liter of free fluoboric acid; boric acid is added and a porous bag thereof is suspended in the bath to ensure its saturation therewith. The bath also contains about 15.0 grams per liter of the AMIDOX C-5 product, about 0.75 gram per liter of 2,4-dichlorobenzaldehyde and about 1.0 gram per liter of 1,2,4-trichlorobenzene. Plating is carried out at a pH of about 1.2 and at room temperature, utilizing a block of tin as the anode and a length of copper wire wound spirally upon a one inch diameter mandrel as the cathode. During the plating operation, the mandrel is rotated in the bath at several speeds to simulate wire plating at rates of from about 200 to 1,800 lineal feet per minute, and the current density at the cathode is varied from about 400.0 to 2,000.0 amperes per square foot. Under all conditions, good quality electrodeposits of tin are produced upon the wire workpiece. Although the plate is somewhat dull at current densities below about 600.0 amperes per square foot, in terms of wire plating criteria the deposit is bright thereabove.

PART B

The procedure of Part A of this Example is repeated utilizing a bath having the composition specified, except that the dichlorobenzaldehyde and trichlorobenzene components are omitted therefrom. The deposits produced are of good quality, but are somewhat duller than those produced in accordance with Part A.

EXAMPLE THREE

PART A

An aqueous plating bath is prepared by admixing with water sufficient quantities of stannous and lead fluoborate concentrate, fluoboric acid, and boric acid, to provide about 55.0 grams per liter of stannous ion, about 25.0 grams per liter of lead ion, about 100.0 grams per liter of fluoboric acid absolute, and 25.0 grams per liter of boric acid. The bath also contains a brightener system consisting of about 15.0 milliliters per liter of the AMIDOX C-5, 6.0 milliliters per liter of ortho-toluidine, about 30.0 milliliters per liter of 37.0 percent formaldehyde, 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene, and about 6.0 milliliters per liter of a 10.0 percent methanol solution of 2,4-dichlorobenzaldehyde. About 7.5 milliliters per liter of a 10.0 percent methanol solution of cresylic acid is also included in the bath, and the pH is less than 1.0. Plating is effected in a Hull cell at room temperature, using as the anode an alloy of 60/40 tin/lead. The bright plating current density range is found to extend from about 10 to more than 120 ASF, and even below 10 ASF the deposits are of good quality, albeit with a slightly milky appearance.

PART B

In a series of barrel plating runs, the same formulation as was described in Part A hereof is employed, the temperature and current density being varied to demonstrate the characteristics of the bath. As a result, it is found that the optimum temperature of operation for this bath is about 70° to 85° Fahrenheit; higher temperatures are found to be less desirable since oxidation of tin to the stannic state is more pronounced and since operation is required within a higher current density range for bright deposits. At current densities of less than about 75.0 ASF, plating efficiency is found to be considerably higher than about 90 percent; at a current density of about 30.0 ASF a nearly eutectic alloy, containing about 64 percent of tin, is produced. Mild agitation during plating is found to result in deposits of excellent appearance, the covering power is outstanding, and the throwing power of the bath appears to be very good, particularly for an acidic system.

PART C

A bath comparable to that of Part A hereof is prepared to contain about 70.0 grams per liter of tin, about 10.0 grams per liter of lead, and about 20.0 milliliters per liter of formaldehyde. Under the same conditions of operation set forth herein the range of current density in which the deposit is bright is found to be about 15.0 to 50.0 ASF; the deposit is analyzed to have about a 90/10 tin/lead composition.

PART D

A bath having the same composition as that set forth in Part A of this Example is prepared, omitting the

formaldehyde and 1,2,4-trichlorobenzene components therefrom; in addition, an equal weight of 2,6-dichlorobenzaldehyde is substituted for the 2,4-dichlorobenzaldehyde, and an equal weight of an ethylene oxide condensate of lauric monoethanolamide (AMIDOX L–2) is substituted for the alkylolamide surfactant employed therein. At room temperature, the deposit is found to be semi-bright from about 1.5 to 12.0 ASF; in the range of about 12.0 to 75.0 ASF the deposit is white but somewhat streaked; and from about 75.0 to about 150.0 ASF the deposit is somewhat brighter, and slightly less streaking is evident. Utilizing the same bath at about 90° Fahrenheit generally improves the quality, and produces a dull-bright deposit at current densities of about 2.0 to 18.0 ASF and a bright hazy deposit from about 18.0 to 100.0 ASF.

PART E

Part D hereof is substantially repeated, with the sole exception that about 5.0 grams per liter of ortho-toluidine and various amounts of a carbonyl-containing compound other than the 2,6-dichlorobenzaldehyde is employed therein. In combination with the ortho-toluidine, equivalent results to those obtained in Part D of this example are realized with (1) about 0.5 gram per liter of benzylidene acetone, (2) about 5.0 grams per liter of 3-hydroxybutanal, (3) about 0.1 gram per liter of thiophene aldehyde, (4) about 0.1 gram per liter of 2,5-dimethoxybenzaldehyde, and (5) about 1.0 gram per liter of anisaldehyde.

PART F

A bath is prepared as in Part A hereof to contain about 50.0 grams per liter of stannous ion, about 25.0 grams per liter of lead ion, about 17.0 grams per liter of the AMIDOX C–5 surfactant, and about 1.3 grams per liter of 1,2,4-trichlorobenzene. Operation at current densities of about 5.0 to 50.0 ASF and at room temperature produces a nominal 60/40 tin/lead alloy deposit which is smooth and exhibits a semi-bright sheen.

PART G

Part A is again repeated utilizing sufficient stannous fluoborate and lead fluoborate to provide about 17.5 and 157.5 grams per liter of stannous ion and lead ion respectively. The bath contains about 15.0 grams per liter of the AMIDOX C–5 surfactant, and about 1.5 gram per liter of the RENEX 650 secondary surfactant referred to in Part A of Example One. Operation at current densities of about 2.0 to 100.0 ASF and at room temperature is found to produce a 10/90 tin/lead alloy deposit that exhibits a slight sheen and has a refined grain structure that is substantially free of treeing.

EXAMPLE FOUR

Sufficient amounts of stannous fluoborate and lead fluoborate are admixed in water to provide about 150.0 grams per liter of stannous ion and about 75.0 grams per liter of lead ion. In addition, the bath also contains about 15.0 grams per liter of AMIDOX C–5 surfactant, about 0.3 gram per liter of 2,4-dichlorobenzaldehyde, about 1.0 gram per liter of 1,2,4-trichlorobenzene, and about 10.0 milliliters per liter of a 37 percent solution of formaldehyde. Utilizing an anode of 60/40 tin/lead alloy and a length of copper wire in the apparatus described in Example Two a relatively bright 60/40 deposit is produced at current densities of about 400.0 to 2,000.0 ASF with the wire moving through the bath at a rate of about 200 to 1,800 lineal feet per minute.

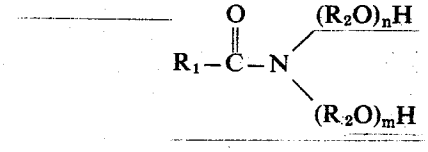
EXAMPLE FIVE

Stannous fluoborate and lead fluoborate are admixed with water in quantities sufficient to provide about 15.0 and 10.0 grams per liter thereof, respectively. The bath also contains about 15.5 grams per liter of the AMIDOX C–5 surface active agent, about 0.78 gram per liter of 2,4-dichlorobenzaldehyde, about 1.0 gram per liter of 1,2,4-trichlorobenzene, and sufficient fluoboric acid to provide about 400.0 grams per liter of the free acid; the pH of the bath is 0.2 or below. Using an anode of 60/40 tin/lead alloy in a Hull cell, and operating at room temperature, bright deposits nominally containing tin and lead in a 60/40 ratio are produced at current densities of about 5.0 to 50.0 ASF. Adding about 0.5 to 3.0 percent by volume of a 37 percent solution of formaldehyde is found to brighten the bath and to render it somewhat less sensitive to variations.

Thus, it can be seen that the present invention provides a novel electroplating bath which is capable of producing highly desirable deposits of tin, lead and tin/lead alloys. The bath operates with good current efficiency and over a broad range of current density to produce a deposit that is smooth, relatively non-porous, uniform, of fine grain structure, and/or bright when so desired; the deposit may be of an optimum composition for soldering in the case of the alloy compositions. The invention also provides a novel method for the production of a high quality metal deposit, which method is rapid, efficient and effective, and which may be conducted under convenient and practical conditions over a broad range of current density. It may, in addition, be effected at high relative speeds between workpiece and bath for wire plating operations.

Having thus described the invention, I claim:

1. An aqueous acid plating bath for the electrodeposition of tin, lead and alloys thereof comprising about 15.0 to 350.0 grams per liter of a metal ion selected from the group consisting of stannous ion, lead ion, and mixtures thereof; about 100.0 to 500.0 grams per liter of a radical selected from the group consisting of fluoborate, fluosilicate sulfamate, and mixtures thereof; and about 10.0 - 25.0 grams per liter of an alkoxylated fatty acid alkylolamide surfactant, said bath having a pH less than about 3.0, said alkylolamide surfactant having the formula



wherein R_1 is a fatty acid alkyl group containing eight to 22 carbon atoms, R_2 is selected from the group ethylene, propylene and mixtures thereof, m is an integer from 0 to 15, n is an integer from 1 to 30, and the sum of m plus n is an integer from 2 to 30.

2. The bath of claim **1** additionally containing about 0.1 to 10.0 grams per liter of a ring halogenated aromatic aldehyde.

3. The bath of claim **1** additionally containing about 2.0 to 15.0 grams per liter of an aromatic amine.

4. The bath of claim 3 wherein said aromatic amine is selected from the group consisting of toluidines and aniline.

5. The bath of claim 3 additionally containing about 0.1 to 10.0 grams per liter of a carbonyl containing compound selected from the group consisting of benzylidene acetone, 3-hydroxybutanal, thiophene aldehyde, benzaldehyde, dimethoxybenzaldehyde, tolualdehyde, cinnamaldehyde, and anisaldehyde.

6. The bath of claim 1 additionally containing about 2.0 to 25.0 grams per liter of a lower aliphatic aldehyde containing 1 to 4 carbon atoms.

7. The bath of claim 1 additionally containing about 0.5 to 3.0 grams per liter of a trichlorinated benzene derivative.

8. The bath of claim 1 wherein said radical of said group is fluoborate, and wherein said pH is about 0.1 to 1.5.

9. The bath of claim 1 wherein said metal ion is lead ion in an amount of at least about 75.0 grams per liter, said bath being substantially free of tin ions.

10. The bath of claim 9 wherein the amount of said lead ion is at least 150.0 grams per liter, wherein said pH is about 0.1 to 1.5, and wherein said bath additionally contains about 0.5 to 5.0 grams per liter of a polyethoxylated alkylphenol secondary surfactant.

11. The bath of claim 1 wherein said metal ion is stannous ion in an amount of at least about 75.0 grams per liter, said bath being substantially free of lead ion.

12. The bath of claim 11 wherein the amount of said stannous ion is about 100.0 to 150.0 grams per liter, and wherein the pH of said bath is about 0.1 to 1.5.

13. The bath of claim 12 additionally including about 0.5 to 3.0 grams per liter of a trichlorinated benzene derivative.

14. The bath of claim 1 wherein said metal ion is a mixture of stannous and lead ions, wherein the amount of said stannous ion is about 10.0 to 180.0 grams per liter and wherein the amount of said lead ion is about 90.0 to 6.0 grams per liter.

15. The bath of claim 14 wherein said radical is fluoborate in an amount of at least about 150.0 grams per liter, wherein said bath contains at least about 50.0 grams per liter of free fluoboric acid and from at least about 10.0 grams per liter of free boric acid to saturation therewith, and wherein said pH is about 0.1 to 1.5.

16. The bath of claim 15 additionally including an aromatic aldehyde selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde present in an amount of about 0.3 to 2.0 grams per liter.

17. The bath of claim 15 additionally including about 0.5 to 3.0 grams per liter of a trichlorinated benzene derivative.

18. The bath of claim 15 additionally including about 0.3 to 2.0 grams per liter of an aromatic aldehyde selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde, and about 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene.

19. The bath of claim 15 additionally including about 2.0 to 15.0 grams per liter of an aromatic amine selected from the group consisting of toluidines and aniline.

20. The bath of claim 19 additionally including about 0.1 to 10.0 grams per liter of a carbonyl-containing compound selected from the group consisting of benzylidene acetone, acetaldol, thiophene aldehyde, benzaldehyde, 2,5-dimethoxybenzaldehyde, tolualdehyde, cinnamaldehyde, and anisaldehyde.

21. The bath of claim 18 additionally including about 2.0 to 25.0 grams per liter of formaldehyde.

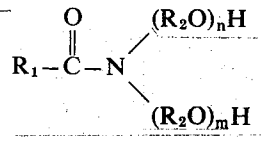
22. The bath of claim 14 wherein the amount of said stannous ion is about 45.0 to 65.0 grams per liter and the amount of said lead ion is about 30.0 to 20.0 grams per liter.

23. The bath of claim 1 wherein said metal ion is a mixture of stannous and lead ion, wherein the amount of said stannous ion is about 10.0 to 30.0 grams per liter and wherein the amount of said lead ion is about 200.0 to 100.0 grams per liter.

24. The bath of claim 23 wherein the amount of stannous ion is about 15.0 to 20.0 grams per liter and wherein the amount of said lead ion is about 175.0 to 150.0 grams per liter, said bath additionally containing about 0.5 to 5.0 grams per liter of a polyethoxylated alkyl phenol secondary surfactant and having a pH of about 0.1 to 1.5.

25. In a method of electroplating tin, lead or mixtures thereof, the steps comprising:

a. preparing an aqueous acid plating bath comprising about 15.0 to 350.0 grams per liter of a metal ion selected from the group consisting of stannous ion, lead ion, and mixtures thereof, at least about 100.0 grams per liter of a radical selected from the class consisting of fluoborate, fluosilicate, sulfamate, and mixtures thereof, and about 10.0 - 25.0 grams per liter of an alkoxylated fatty acid alkylolamide surfactant, said bath having a pH less than about 3.0, said alkylolamide surfactant having the formula



wherein R_1 is a fatty acid alkyl group containing eight to 22 carbon atoms, R_2 is selected from the group ethylene, propylene and mixtures thereof, m is an integer from 0 to 15, n is an integer from 1 to 30, and the sum of m plus n is an integer from 2 to 30;

b. maintaining said bath at a temperature of about 50° to 150° Fahrenheit;

c. immersing in said bath a workpiece having a metallic surface and at least one anode of a metal selected from the class consisting of tin, lead, and alloys thereof; and

d. applying a voltage across said anode and said workpiece to deposit said metal on said metallic surface, said voltage providing a current density of about 2.0 to 2,000.0 amperes per square foot at the surface of said workpiece.

26. The method of claim 25 wherein said bath contains at least 150.0 grams per liter of lead ion and is substantially free of tin ions, wherein said metal of said class is lead, and wherein said current density is less than about 100.0 amperes per square foot.

27. The method of claim 26 wherein said bath additionally contains about 0.5 to 5.0 grams per liter of a polyethoxylated alkyl phenol secondary surfactant, wherein said radical of said class is fluoborate, and wherein said pH is about 0.1 to 1.5.

28. The method of claim 25 wherein said bath contains about 100.0 to 150.0 grams per liter of stannous ion and is substantially free of lead ion, wherein said metal of said class is tin, wherein said current density is greater than about 400.0 amperes per square foot, and wherein said workpiece and bath are moved relative to one another at a rate of at least about 150 lineal feet per minute.

29. The method of claim 28 wherein said bath additionally contains about 0.3 to 2.0 grams per liter of an aromatic aldehyde selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde and about 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene, wherein said radical of said class is fluoborate, and wherein said pH is about 0.1 to 1.5.

30. The method of claim 25 wherein said bath contains about 45.0 to 65.0 grams per liter of stannous ion and about 30.0 to 20.0 grams per liter of lead ion, wherein said metal of said class is a tin/lead alloy, wherein said pH is about 0.1 to 1.5, and wherein said current density is less than 100.0 amperes per square foot.

31. The method of claim 30 wherein said bath additionally contains about 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene and wherein said current density is about 5.0 to 50.0 amperes per square foot.

32. The method of claim 30 wherein said bath additionally contains about 0.3 to 2.0 grams per liter of an aromatic aldehyde selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde and wherein said radical of said class is fluoborate.

33. The method of claim 32 wherein said temperature is above about 80° Fahrenheit.

34. The method of claim 32 wherein said bath additionally contains about 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene, about 2.0 to 25.0 grams per liter of formaldehyde, and about 2.0 to 15.0 grams per liter of an aromatic amine selected from the group consisting of toluidines and aniline.

35. The method of claim 30 wherein said bath additionally contains at least 0.1 to 10.0 grams per liter of a carbonyl-containing compound selected from the group consisting of benzylidene acetone, 3-hydroxybutanal, thiophene aldehyde, benzaldehyde, 2,5-dimethoxy-benzaldehyde, tolualdehyde, cinnamaldehyde, and anisaldehyde, and about 2.0 to 15.0 grams per liter of an aromatic amine selected from the group consisting of toluidines and aniline

36. The method of claim 25 wherein said bath contains about 15.0 to 20.0 grams per liter of stannous ion and about 175.0 to 150.0 grams per liter of lead ion, wherein said metal of said class is a tin/lead alloy, wherein said bath additionally contains about 0.3 to 2.0 grams per liter of an aromatic aldehyde selected from the group consisting of 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde, about 0.5 to 3.0 grams per liter of 1,2,4-trichlorobenzene, and about 2.0 to 25.0 grams per liter of formaldehyde, wherein said pH is about 0.1 to 1.5, wherein said current density is greater than about 400.0 amperes per square foot, and wherein said workpiece and bath are moved relative to one another at a rate of at least about 150.0 lineal feet per minute.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,769,182 Dated October 30, 1973

Inventor(s) Grace F. Hsu

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the abstract page in the caption, the name of the inventor(s) should be changed from Beckwith et al. to Hsu;

On the abstract page in the title portion at item [75], the designation of inventor(s) should be changed from Merton M. Beckwith, Rockville; Grace F. Hsu, Vernon, both of Conn. to read Inventor: Grace F. Hsu, Vernon, Conn.

Signed and sealed this 30th day of April 1974.

(SEAL)
Attest:

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Attesting Officer

C. MARSHALL DANN
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