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(54) TIN/LEAD ELECTROPLATING BATHS

(71) We, KENVERT INTERNATIONAL CORPORATION, a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 210 East Main Street, Rockville, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electroplating baths and more particularly to acid electroplating baths for electrodepositing tin, lead and alloys of tin and/or lead. As is well known, electrodeposits of tin and/or lead are employed in a wide variety of decorative and functional applications. A wide variety of formulations for the production of such deposits have been proposed but, 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.

Electrodeposited tin/lead alloys of different compositions are valuable in a number of applications including the provision of bearing contact surfaces (for which a 7/93 tin/lead alloy is typically used) and the provision of surfaces for soldering such as on printed circuit boards (for which 60/40 tin/lead alloys are desired), and in this case a bath that is capable of producing a high quality tin/lead deposit having a composition at or near the eutectic value for the alloy (about 63/37), as is optimum for soldering purposes, is desirable. Effective compositions for producing bright or semi-bright alloy electrodeposits have not been available commercially, and there is a widespread demand for a practical way of producing such deposits on articles of various types for both technical and also aesthetic reasons. It is also

desirable that such deposits retain their solderability over extended periods of time, and either be resistant to discoloration or be readily treated to prevent such discoloration.

It is an object of the present invention to provide an electroplating bath which is capable of producing good deposits of tin, lead or alloys of tin and/or lead.

It has now been found, in accordance with the present invention that deposits of tin, lead or alloys of tin and/or lead may be electrodeposited from an acid electroplating bath containing stannous and/or lead ions; fluoroborate, fluosilicate and/or sulfamate radicals; together with a surface active component comprising a nonionic polyalkoxylated surface active compound either alone or in combination with other ingredients. More specifically, the nonionic polyalkoxylated compound should be used in admixture with two other components, namely a lower aliphatic aldehyde and an aromatic aldehyde, but when it is an alkoxylated fatty acid alkylolamide these two latter ingredients are not necessarily present, although, of course, either of both may be present.

According to the invention, therefore, there is provided an aqueous acid plating bath for the electrodeposition of tin, lead or alloys of tin and/or lead said bath having a pH of less than 3.0 and comprising from 15.0 to 350.0 grams per litre of metal ions which are stannous ions and/or lead ions; from 100.0 to 500.0 grams per litre of acid radicals which are fluoborate, fluosilicate and/or sulfamate radicals; and a surface active component comprising at least 5.0 grams per litre of a nonionic polyalkoxylated surface active compound and which is (a) an alkoxylated fatty acid alkylolamide surface active agent or (b) a mixture of at least 5.0 grams per litre of a nonionic polyalkoxylated compound and a brightener component comprising at least 4.0 grams per litre of a lower aliphatic aldehyde containing from 1 to 4 carbon atoms and at least 0.25 grams per litre of an aromatic aldehyde.

[Price 25p]

Price 33p

When a bath does not include the combination brightener component set forth in (b) above, it must utilize the alkoxyated fatty acid alkylolamide surfactant component, preferably in an amount of 5.0 to 50.0 grams per litre. It will be appreciated that the alkylolamide surfactant may be used in admixture with other types of nonionic poly-alkoxyated surfactant.

In the plating process, the bath is maintained at a temperature of about 10° to 66° Centigrade, and there are immersed therein a workpiece having a metallic surface and at least one anode of tin, lead or an alloy thereof. Thereafter a voltage is applied across the anode and workpiece to deposit the metal of the bath on the metallic surface, and the applied voltage provides a current density of about 2.0 to 2,000.0 amperes per square foot at the surface of the workpiece.

When the bath is intended to provide a tin/lead alloy deposit, the current density is preferably from 10 to 200 amperes per square foot, and there may be employed anodes which are of tin/lead alloy, or separate anodes of tin and lead with the current apportioned between the anodes to deposit the tin and lead in the desired proportions.

In instances in which the bath contains at least 150.0 grams per litre of lead ions and is substantially free from tin ions, or in which it contains from 45.0 to 65.0 grams per litre of stannous ions and about 30.0 to 20.0 grams per litre of lead ions, the current density at the workpiece is preferably less than 100.0 amperes per square foot. When the bath contains from 100.0 to 150.0 grams per litre of stannous ions and is substantially free from lead ions, or when it contains from 15.0 to 20.0 grams per litre of stannous ions and from 175.0 to 150.0 grams per litre of lead ions, the current density is preferably greater than 400.0 amperes per square foot and, most desirably, it is at least 600.0 amperes per square foot; the workpiece and the bath may be moved relative to each other at a rate of at least 150.0 linear 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 method of the invention, and in cost cases the pH of the bath employed will preferably be from 0.5 to 1.5.

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 a lesser degree, the technique employed, and conditions of the operation, etc. In any event, to obtain satisfactory results the concentration of the cation to be electrodeposited (be in tin, lead, or a mixture thereof) must be from about 15.0 to 350.0 grams per litre because

amounts outside of this range will result in poor efficiency, sludging or precipitation 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 75.0 grams per litre; most desirably, when lead is employed alone it will be present in an amount of at least 150.0 grams per litre and when tin is the only cation present its concentration should be from 100.0 to 150.0 grams per litre.

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 from 5.0 to 180.0 and from 90.0 to 6.0 grams per litre, respectively. Usually, the amounts will be from 5.0 to 80.0 grams per litre of stannous ion and from 85.0 to 10.0 grams per litre lead ions (in which case a tin/lead anode used in conjunction with the bath will probably comprise about 60% by weight of tin and about 40% by weight of lead); desirably, such a bath will contain from 45.0 to 65.0 grams per litre of stannous ions and from 30.0 to 20.0 grams per litre of lead ions. On the other hand, when the alloy deposit is to contain a predominant amount of lead, the bath advantageously contains from 10.0 to 30.0 grams per litre of stannous ions and from 200.0 to 100.0 grams per litre of lead ions; preferably, the concentrations of the respective metals in such a bath will be from 15.0 to 20.0 and from 175.0 to 150.0 grams per litre.

When the amount of stannous ions exceeds that of the lead ions, 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 from 53.0 to 57.0 grams per litre of stannous ions and from 27.0 to 23.0 grams per litre of lead ions.

The electrolyte radical is fluoborate, fluosilicate, sulfamate, or mixtures thereof, although other non-interfering radicals may be present as the result of using salts thereof to furnish all or a portion of the tin and lead ions in the bath. Thus, the electrolyte radicals may be provided as the acids or as salts of non-interfering cations. It should be appreciated that the terms "fluoborate", "fluosilicate", and "sulfamate" are used generally 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 from 100.0 to 500.0 grams per litre of the fluoborate radical; preferably, not less than 150.0 grams per litre thereof. Typically, such a bath

will also contain at least 50.0 grams per litre of free fluoboric acid and at least 10.0 grams per litre of free boric acid (and have a pH of less than 1.0), 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.

In preparing tin/lead solder plate, a typical "make-up" formula (brightening system and additives omitted) for a litre bath, that has performed well, is as follows (percentages expressed being by weight):

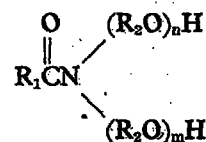
	Stannous Fluoborate Concentrate	272 grams
	49.6% Stannous Fluoborate	
	1.8% Fluoboric Acid	
20	2.0% Boric Acid	
	Lead Fluoborate Concentrate	92.8 grams
	51% Lead Fluoborate	
	0.6% Fluoboric Acid	
	1.9% Boric Acid	
25	Fluoboric acid (49%)	142 milliliters
	Boric Acid	18.3 grams

The foregoing formulation provides about 60.0 grams per litre of total tin (about 55.0 grams per litre of stannous ion and about 5.0 grams per litre of stannic ion) about 25.0 grams per litre of lead ion, about 100.0 grams per litre of fluoboric acid (absolute), and about 25.0 grams per litre of boric acid.

In accordance with one embodiment of the present invention, the foregoing type of make-up formulation (be it of the fluoboric, fluosilicate, or sulfamate variety) must also contain a brightened system comprising of at least 5.0 grams per litre of nonionic polyoxyalkylated surfactant, at least 4.0 grams per litre of a lower aliphatic aldehyde, and at least 0.25 grams per litre of an aromatic aldehyde. Preferably, the amounts of the foregoing components will be from 10.0 to 30.0, from 5.0 to 15.0 and from 0.4 to 1.5, grams per litre, respectively.

As regards the specific composition of the nonionic surfactant for tin/lead baths containing the combination brightener component, any surface active polyoxylated compound that is soluble in the bath may be employed, and a wide variety of such materials are commercially available under a number of different trade names. However, the polyethoxylated fatty acid monoalkanolamides and related amines, and the polyethoxylated alkylphenols have performed particularly effectively. An example of the polyethoxylated alkylphenol surfactants that may be used is the ethoxylated nonylphenol derivative sold by Onyx Chemical Company of Jersey City, New Jersey, under the trademark Neutronyx 675.

When the bath is used for plating tin or lead alone or used without a combination brightener system (the lower aliphatic aldehyde and aromatic aldehyde), the bath must contain a polyoxyalkylated fatty acid alkylolamide surfactant, and such surfactants are desirably used in all the baths of the present invention. The polyoxyalkylated fatty acid alkylolamide surfactant is suitably present in an amount of from 5.0 to 50.0 grams per litre, and preferably in an amount of from 10.0 to 25.0 grams per litre; at concentrations lower than 10.0 grams per litre there is some tendency for the deposit to darken and to become porous, whereas concentrations of more than 25.0 grams per litre tend to cause coarseness. Alkylolamide surfactants that are suitable for use in the baths of the invention may be represented by the formula:



in which R_1 is a fatty acid alkyl group containing from 8 to 22 carbon atoms, each of R_2 is an ethylene or propylene group, m is an integer of from 0 to 15, n is an integer of from 1 to 30, and the sum of m and n is an integer of from 2 to 30; generally, when m is other than zero it will be equal to n , unless n is from 16 to 30. Commercial products which may be employed to furnish the alkylolamide surfactant include the fatty acid derivatives sold by Stepan Chemical of Northfield, Illinois 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 particularly 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 used to provide this component of the baths is Armour Industrial Chemical Company of Chicago, Illinois, 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 the number of moles of ethylene oxide that are believed to be present in a molecular 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.

5 In some of the baths falling within the scope of the present invention, a secondary surfactant may be utilized in addition to and in combination with the fatty acid alkylolamide derivative to produce optimum properties in the deposit. Examples of such secondary surfactants are polyalkoxylated alkylphenols, and especially the condensates of alkylphenols having from 6 to 12 carbon atoms in the alkyl chain with an alkylene oxide, e.g. ethylene oxide, and/or propylene oxide. Generally, these products will contain from 5 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, Delaware under the designations Renex 650 and Renex 697 (Regd. Trade Marks); the product sold by General Aniline and Film Corporation of New York, New York, 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, New Jersey. The amount of the secondary surfactant employed will generally be from 0.5 to 5.0 grams per litre, and normally about 1.5 grams per litre thereof will be most satisfactory. Mixtures of different types of secondary surfactants may also be used.

35 In most instances, the baths will contain one or more carbonyl-containing compounds to increase the level of the brightness of the deposit.

40 A variety of different types of ring compounds may be used as carbonyl-containing compounds such as the ring halogenated benzaldehydes, benzylidene acetone, 3-hydroxybutanal, thiophene aldehyde, benzaldehyde, 2,5 - dimethoxybenzaldehyde, tolu-aldehyde, cinnamaldehyde, and anisaldehyde. The ring halogenated benzaldehydes are preferred, and particularly desirable results have been obtained using either 2,4 - dichlorobenzaldehyde, or 2,6 - dichlorobenzaldehyde. It has also been found that the presence of from 2.0 to 15.0, and preferably from 3.0 to 8.0 grams per litre of a primary or secondary aromatic amine (for example a toluidine, such as ortho 1 toluidine, meta - toluidine or N-ethyl - ortho - toluidine or aniline) is highly desirable to obtain optimum results in the baths of the present invention using carbonyl compounds 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 carbonyl compounds will generally be at least

0.1 gram per litre; usually, at least 0.3 gram per litre thereof will yield desirable results. More than about 10.0 grams per litre will, in most cases, be without additional benefit; the preferred upper limit is about 2.0 grams per litre from the standpoint of economy and minimizing unnecessary concentrations of components.

When the bath is an alkylolamide containing both and contains a carbonyl compound or other brightening agent, it will usually be desirable to also include from 2.0 to 25.0 grams per litre of a lower aliphatic aldehyde (i.e. containing 1 to 4 carbon atoms). Although acetaldehyde, butyraldehyde and propionaldehyde may be employed, formaldehyde is preferred. The presence of the lower aliphatic aldehyde appears to widen the range of current density over which a bright deposit is obtained and to otherwise improve operation.

An additional brightening agent 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 from 0.5 to 3.0 grams per litre 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.

In addition to the foregoing compounds, and in accordance with the preferred embodiments, various other additives may be included in the plating formulation. A particularly desirable additive is a compound furnishing an amine group, including both aliphatic and aromatic amines. Although aliphatic compounds such as butylamine have been effective, particularly outstanding improvements have been noted to result from the inclusion of aromatic amines, and especially from the use of ortho-toluidine, meta-toluidine and aniline.

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 and beta-naphthol. When used, these additives should usually be included in amounts of from 0.5 to 7.5 grams per litre, and it has been found that from 0.5 to 5.0 grams per litre 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 such as citric acid, malic acid or the aminopolyacetic acids (e.g. ethylenediamine tetraacetic acid, ethylenetriamine pentaacetic acid, nitrotriacetic acid). Such chelating agents, when employed, are generally included in

an amount of from 5.0 to 20.0 grams per litre.

Since some of the suitable brighteners and other components which may be desirable by 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 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.

A typical brightener system found to produce outstanding bright solder plate deposits, in combination with the typical "make-up" formulation hereinbefore described, has the following composition, on a litre basis:

	millilitres
Polyethoxylated fatty acid mono-ethanolamide surfactant (Amidox C-5)	15
Ortho toluidine	16
Formaldehyde (37 weight % in water)	30
2,4 - Dichlorobenzaldehyde (10 weight % in methanol)	6

Baths 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). The preferred tin/lead solder plate baths have an operable range of about 10.0 to 200.0 amperes per square foot (ASF) and preferably about 20.0 to 120.0 ASF, with a narrower range of 25.0 to 35.0 ASF being most desirable for the production of deposits having a substantially eutectic composition, i.e. comprising from 62.0 to 64.0 percent by weight of tin and from 38.0 to 36.0 percent by weight of lead. The plating efficiency is generally quite high and will range up to about 95 percent under optimum conditions, based upon the theoretical rate of deposition, and bright deposits of excellent quality can be best be produced at

a bath efficiency in excess of 70 percent. The applied voltage for solder plate baths should be from 0.2 to 5.0 volts and preferably from 0.5 to 4.0 volts. In rack and barrel plating operations using alkylolamide baths, 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.

The plating efficiency of all the alkylolamide baths 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 from 0.2 to 10.0 volts for those baths containing only lead or tin ions, and preferably plating will be carried out at from 0.5 to 5.0 volts; the most desirable voltage level depending upon the plating technique and conditions employed.

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. Excessively high rates of agitation are undesirable because they can cause excessive consumption of the bath and impose limitations upon the current densities at which brightness is achieved. Not only is some agitation of the bath itself desirable but agitation of the cathode may be beneficial in obtaining a uniform plate and enabling extension of the range of satisfactory current density. of course, in wire plating operations the work-piece and bath move rapidly relative to one another and the bath of the present invention may be chosen to operate at wire speeds in excess of about 150, and preferably above 200, linear feet per minute.

The baths should be operated at a temperature of from 10° to 66°, and preferably from 16° to 32° Centigrade; temperatures above about 27° Centigrade are often most desirable. Operation below about 10° Centigrade tends to be inefficient and to produce undesirable deposits. 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 and lower 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 alloys 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 polypropylene) and other conventional filtering material.

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 sulfuric 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 work-piece.

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.

The process is adapted to still plating and barrel plating apparatus with equal efficacy, and may be used for strip and wire. Use of the tin/lead solder plate bath and process is particularly significant with respect to connector strip and printed circuit boards, because of the excellent solderability of the plate produced.

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 struc-

tures without undesirable crystal growth (i.e. treeing). In addition, the deposits are fully adherent to the surface of the work-piece, and the bath composition may be such that every heavy deposits, i.e., those of about 1 to 4 mils in thickness, are free from peeling and cracking.

In order that the invention may be well understood the following Examples are given by way of illustration only. In the Examples 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 millilitre 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 litre of lead metal, about 15.0 grams per litre of free fluoboric acid, about 22.5 grams per litre of free boric acid and a pH less than about 1.5. Also included in the bath is about 15.0 grams per litre of a coconut fatty acid alkylolamide surfactant containing about 5 moles of ethylene oxide per mole thereof (sole by Stepan Chemical Company or Northfield, Illinois as Amidox C-5), and about 1.5 grams per litre 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 plating is effected with a current of two amperes for five 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 colour, 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 is employed at temperatures of 80°, 90°, 100° and 130° Fahrenheit, and at voltages of 3.5, 3.5, 3.0, 3.0, and 2.75 volts respectively. The increase in temperature refines the grain structure of the deposit at current densities above about 50.0 ASF, and 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 good quality and free from porosity at current densities of from 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 litre of stannous ion and about 140.0 grams per litre 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 litre of the Amidox C-product, about 0.75 gram per litre of 2,4 - dichlorobenzaldehyde and about 1.0 gram per litre 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 linear 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 work-pieces. 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 or thereabove.

Part B

The procedure of Part A 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 55.0 grams per litre of stannous ion, 25 gm/litre lead ion, 100.0 grams per litre of fluoboric acid and 25.0 grams per litre of boric acid. The bath also contains a brightener system consisting of about 15.0 millilitres per litre of the Amidox C-5, 16.0 millilitres per litre of orthotoluidine, about 30.0 millilitres per litre of 37.0 percent formaldehyde, and about 6.0 millilitres per litre of a 10.0 percent methanol solution of 2,4 - dichlorobenzaldehyde. About 7.5 millilitres per litre 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 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 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 the 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 having the same composition as that of Part A except that it contains about 70.0 grams per litre of tin, about 10.0 grams per litre of lead, and about 20.0 millilitres per litre of 37% formaldehyde. Under the same conditions of operation set forth therein the range of current density in which the deposit is bright and 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 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 from 2.0 to 18.0 ASF and a bright hazy deposit from 18.0 to 100.0 ASF.

Part E

Part D is substantially repeated, with the sole exception that about 5.0 grams per litre 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 are realized with (1) about 0.5 gram per litre of benzylidene acetone, (2) about 5.0 grams per litre of 3-hydroxybutanal, (3) about 0.1 gram per litre of thiophene aldehyde, (4) about 1.0 gram per litre of 2,5-dimethoxybenzaldehyde, and (5) about 1.0 gram per litre of anisaldehyde.

Part F

A bath is prepared as in Part A to contain about 50.0 grams per litre of stannous ion, about 25.0 grams per litre of lead ion, about 17.0 grams per litre of the Amidox C-5 surfactant, and about 1.3 grams per litre of 1,2,4 - trichlorobenzene. Operation at current densities of from 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 litre of stannous ion and lead ion respectively. The bath contains about 15.0 grams per litre of the Amidox C-5 surfactant, and about 1.5 gram per litre 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 sheet 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 litre of stannous ion and about 75.0 grams per litre of lead ion. In addition, the bath also contains about 15.0 grams per litre of Amidox C-5 surfactant; about 0.3 gram per litre of 2,4 - dichlorobenzaldehyde, about 1.0 gram per litre of 1,2,4 - trichlorobenzene, and about 10.0 millilitres per litre 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 from 200 to 1,800 linear feet per minute.

Example Five

Stannous fluoborate and lead fluoborate are admixed with water in quantities sufficient to provide about 15.0 to 10.0 grams per litre thereof, respectively. The bath also contains about 15.5 grams per litre of the Amidox C-5 surface active agent, about 0.78 gram per litre of 2,4 - dichlorobenzaldehyde, about 1.0 gram per litre of 1,2,4 - trichlorobenzene, and sufficient fluoboric acid to provide about 400.0 grams per litre 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 0.3 percent by volume of a 37 percent solution of formaldehyde is found to brighten the bath.

Thus, it can be seen that the present invention provides an 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 method of the invention provides work-pieces having at least relatively bright tin/lead alloy electrodeposits in which the composition is at or near the eutectic point for such alloys, as is optimum for soldering. The invention also provides a 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.

WHAT WE CLAIM IS:—

1. An aqueous acid electroplating bath for

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 alkylol-
 5 amide surfactant employed therein. At room temperature, the deposit is found to be semi-bright from about 1.5 to 12.0 ASF; in the
 10 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
 15 the quality, and produces a dull-bright deposit at current densities of from 2.0 to 18.0 ASF and a bright hazy deposit from 18.0 to 100.0 ASF.

Part E

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

Part F

35 A bath is prepared as in Part A to contain about 50.0 grams per litre of stannous ion, about 25.0 grams per litre of lead ion, about 17.0 grams per litre of the Amidox C-5 surfactant, and about 1.3 grams per
 40 litre of 1,2,4 - trichlorobenzene. Operation at current densities of from 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

45 Part A is again repeated utilizing sufficient stannous fluoborate and lead fluoborate to provide about 17.5 and 157.5 grams per litre of stannous ion and lead ion respectively.
 50 The bath contains about 15.0 grams per litre of the Amidox C-5 surfactant, and about 1.5 gram per litre of the Renex 650 secondary surfactant referred to in Part A of Example One. Operation at current densities
 55 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 sheet and has a refined grain structure that is substantially free of treeing.

60

Example Four

Sufficient amounts of stannous fluoborate and lead fluoborate are admixed in water to

provide about 150.0 grams per litre of stannous ion and about 75.0 grams per
 65 litre of lead ion. In addition, the bath also contains about 15.0 grams per litre of Amidox C-5 surfactant, about 0.3 gram per litre of 2,4 - dichlorobenzaldehyde, about 1.0 gram per litre of 1,2,4 - trichlorobenzene, and
 70 about 10.0 millilitres per litre 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
 75 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 from 200 to 1,800 linear feet per minute.

Example Five

Stannous fluoborate and lead fluoborate are
 80 admixed with water in quantities sufficient to provide about 15.0 to 10.0 grams per litre thereof, respectively. The bath also contains about 15.5 grams per litre of the Amidox C-5 surface active agent, about 0.78 gram
 85 per litre of 2,4 - dichlorobenzaldehyde, about 1.0 gram per litre of 1,2,4 - trichlorobenzene, and sufficient fluoboric acid to provide about 400.0 grams per litre of the free acid; the pH of the bath is 0.2 or below. Using an
 90 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.
 95 Adding about 0.5 to 0.3 percent by volume of a 37 percent solution of formaldehyde is found to brighten the bath.

Thus, it can be seen that the present
 100 invention provides an 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
 105 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 method of the invention provides work-pieces having at least relatively bright tin/lead alloy electrodeposits in which the composition is at or near the eutectic point for such alloys, as is optimum
 110 for soldering. The invention also provides a 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
 115 may, in addition, be effected at high relative speeds between workpiece and bath for wire plating operations.

WHAT WE CLAIM IS:—

1. An aqueous acid electroplating bath for 125





- electrodepositing tin, lead or an alloy of tin and/or lead which bath has a pH of less than 3.0 and comprises from 15.0 to 350.0 grams per litre of metal ions which are stannous and/or lead ions; from 100.0 to 500.0 grams per litre of acid radicals which are fluoborate, fluosilicate and/or sulfamate radicals; and a surface active component comprising at least 5.0 grams per litre of a nonionic polyalkoxylated surface active agent and which is (a) an alkoxylated fatty acid alkylolamide surface active agent or (b) a mixture of at least 5.0 grams per litre of a nonionic polyalkoxylated surface active agent and a brightener component comprising at least 4.0 grams per litre of a lower aliphatic aldehyde containing from 1 to 4 carbon atoms and at least 0.25 grams per litre of an aromatic aldehyde.
2. A bath as claimed in claim 1 in which the nonionic surface active component is an alkoxylated fatty acid alkylolamide present in an amount of from 5.0 to 50.0 grams per litre.
3. A bath as claimed in claim 2 in which the fatty acid alkylolamide is present in an amount of from 10 to 25.0 grams per litre.
4. A bath as claimed in claim 2 or claim 3 containing from 5.0 to 180.0 grams per litre of stannous ions and from 90.0 to 6.0 grams per litre of lead ions.
5. A bath as claimed in any one of claims 2-4 containing at least 75.0 grams per litre of lead ion and which is substantially free from tin ions.
6. A bath as claimed in claim 5 containing at least 150.0 grams per litre of lead ion.
7. A bath as claimed in any one of claims 2-4 containing at least 75.0 grams per litre of stannous ion and which is substantially free from lead ions.
8. A bath as claimed in claim 7 containing from 100.0 to 150.0 grams per litre of stannous ions.
9. A bath as claimed in any one of claims 2-8 containing from 0.1 to 10.0 grams per litre of a carbonyl-containing compound which is benzylidene acetone, 3-hydroxybutanol, thiophene aldehyde, benzaldehyde, 2,5 - dimethoxybenzaldehyde, tolualdehyde, cinnamaldehyde or anisaldehyde.
10. A plating bath as claimed in any one of claims 2-9 containing from 2.0 to 25.0 grams per litre of a lower aliphatic aldehyde containing from 1 to 4 carbon atoms.
11. A plating bath as claimed in any one of claims 2-10 in which said surface active component comprises a mixture of the fatty acid alkylolamide and from 0.5 to 5.0 grams per litre of a polyalkoxylated alkylphenol surface active component.
12. A plating bath as claimed in claim 1 containing from 5.0 to 80.0 grams per litre of stannous ion and from 85.0 to 10.0 grams per litre of lead ion and in which the surface active component comprises a mixture of surface active agent and brightener component.
13. A plating bath as claimed in claim 1 or claim 12 in which said surface active component comprises from 10.0 to 30.0 grams per litre of polyalkoxylated surface active compound, from 5.0 to 15.0 grams per litre of lower aliphatic aldehyde and from 0.4 to 1.5 grams per litre of aromatic aldehyde.
14. A bath as claimed in any one of claims 1, 12 and 13 in which the nonionic surface active agent is an ethyloxyated fatty acid monoalkylolamide or an ethoxyated alkylphenol.
15. A bath as claimed in any one of the preceding claims in which the radical is fluoborate and the bath contains at least 150 grams per litre thereof.
16. A bath as claimed in claim 15 containing at least 50.0 grams per litre of free fluoboric acid and at least 10.0 grams per litre of free boric acid and having a pH of less than 1.0.
17. A bath as claimed in any one of the preceding claims containing a ring halogenated aromatic aldehyde.
18. A bath as claimed in claim 17 in which the ring halogenated aromatic aldehyde is 2,4-dichlorobenzaldehyde or orthochlorobenzaldehyde.
19. A bath as claimed in any one of claims 1-16 also containing from 2.0 to 15.0 grams per litre of a primary or secondary aromatic amine.
20. A bath as claimed in claim 19 in which said aromatic amine is a toluidine or aniline.
21. A bath as claimed in any one of the preceding claims also containing from 0.5 to 3.0 grams per litre of a trichlorinated benzene derivative.
22. A bath as claimed in any one of the preceding claims containing from 0.5 to 7.5 grams per litre of a further additive which is peptone, resorcinol, glue, gelatine, beta-naphtol and/or polyvinyl alcohol, or from 0.5 to 5.0 grams per litre of cresylic acid.
23. A bath as claimed in any one of the preceding claims in which the lower aliphatic aldehyde is formaldehyde.
24. A bath as claimed in claim 1 substantially as hereinbefore described and with reference to the Examples.
25. A method of electroplating a workpiece having a metallic surface which comprises immersing said workpiece and at least one anode of a metal which is tin, lead or an alloy thereof, in a bath as claimed in claim 1, maintained at a temperature of from 10 to 66°C, and applying a voltage across said anode and said workpiece to

deposit tin and/or lead on said metallic surface.

26. A method as claimed in claim 25 in which the bath contains from 45 to 65.0 grams per litre of stannous ion and from about 30.0 to 20.0 grams per litre of lead ion, the bath also contains from 10.0 to 25.0 grams per litre of the alkylolamide surface agent and the current density of plating is less than 100.0 grams per square foot.

27. A method as claimed in claim 25 in which the bath has the composition defined in claim 12.

28. A method as claimed in claim 27 in which said anode contains about 60.0 percent by weight of tin and about 40.0 percent by weight of lead.

29. A method as claimed in claim 27 in which at least two anodes are immersed in said bath, one of said anodes consisting essentially of tin and the other of said anodes consisting essentially of lead and wherein said method includes the step of apportioning the current between said anodes so as to deposit tin and lead in the desired proportions upon the workpiece.

30. A method as claimed in claim 27 in which the current density of plating is from 25 to 35 amperes per square foot to produce a tin/lead alloy having a composition

of from 62.0 to 64.0 percent by weight of tin and from 38.0 to 36.0 percent by weight of lead.

31. A method as claimed in claim 25 in which the bath has the composition specified in claim 2.

32. A method as claimed in claim 31 in which said bath has the composition specified in claim 6 and the current density is less than 100.0 amperes per square foot.

33. A method as claimed in claim 31 wherein the bath has the composition specified in claim 8 and the current density of plating is more than about 400.0 amperes per square foot, and the workpiece and bath are moved relative to each other at a rate of at least 150 linear feet per minute.

34. A method as claimed in any one of claims 27—33 in which the bath has the composition defined in any one of claims 17—23.

35. A method as claimed in claim 27 substantially as hereinbefore described and with reference to the Example.

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