

[54] **BRIGHT SOLDER PLATING**

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

[56] **References Cited**

UNITED STATES PATENTS

3,661,730 5/1972 Nishihara 204/43 S

3,730,853 5/1973 Sedlacek et al. 204/43 S
3,749,649 7/1973 Valayil 204/43 S

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Arthur E. Kluegel

[57]

ABSTRACT

Disclosed is a method and composition for electroplating a layer of bright solder on a base metal. In addition to soluble divalent tin and lead salts, the bath contains formaldehyde, an aryl primary amine, a condensation product of an aromatic aldehyde and an aromatic amine and a polynuclear aromatic disulfonic acid. Deposits obtained by this bath are not only mirror bright, but exhibit no haze. An important advantage is that the solderability of the deposit may be correlated to its physical appearance.

7 Claims, No Drawings

BRIGHT SOLDER PLATING

BACKGROUND OF THE INVENTION

This invention relates to the electrodeposition of solder on a base metal. More specifically, it relates to the electrodeposition of mirror bright solder.

The two most common methods of obtaining a layer of solder on a substrate are melt-plating and electroplating. The melt-plating technique is undesirable for many applications because of the high temperatures required and because the thickness of the deposited layer is uneven and difficult to control. As a result of these shortcomings, electroplating techniques have become more and more important particularly with the advent of the printed circuit industry. Conventional techniques for electroplating solder provide an electrolyte containing divalent tin and divalent lead, commonly as the fluoborate salts, in addition to excess fluoboric acid and formaldehyde. Summaries of both the electroplating and melt-plating processes are set forth in U.S. Pat. No. 3,661,730, the content of which is incorporated herein by reference.

SUMMARY OF THE INVENTION

The present invention provides an aqueous acidic composition suitable for plating a bright tin-lead alloy of high solderability. In addition, it provides a method of plating such an alloy on a base metal surface.

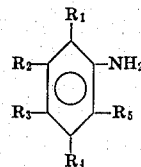
One of the major problems in solder plating is that slight variations in the bath composition, particularly variations in the ratio of the tin to lead in the bath, will result in unsatisfactory products. Specifically, if the tin and lead are not within the proper ratios, the resulting alloy will not have the desired crystal structure and, as a result, when melted, the deposit will not effectively solder the base metal to a second metal. In the past, the only reliable means for determining whether a given deposit was, in fact, solderable was to melt an actual plated sample and test the sample for adhesion. The present invention, in addition to providing a mirror-bright solder plate, also provides a means for visually determining whether the deposit is acceptable without actually melting it. When the bright, low-haze deposits of our invention are obtained, good solderability can be reliably predicted. This is a valuable feature from the quality control standpoint.

The plating composition of this invention contains between 3.5 and 60 grams per liter of divalent tin, preferably between 12 and 30 grams per liter. It also contains divalent lead in a range of between 30 and 45 weight percent, based on the total of the tin and lead in the bath. Since lead is insoluble in the presence of most anions, care must be taken not to include any anions in the bath which would precipitate the lead. While other soluble compounds may be used, the preferred compound to be added to the bath are the fluoborate salts of tin and lead. Less preferred are the methane sulfonate salts. The pH of the bath should be less than about 1, and when fluoborate salts are employed, the pH may conveniently be lowered by the addition of fluoboric acid. Fluosilicic acid, and other similar complex acids may also be employed. Again, the primary requirement of the acid employed is that it must not contribute any interfering anions to the bath. Where the ratio of lead to tin is not within the above-mentioned range, low solderability can normally be expected after melting since the crystal structure will be

altered as a result of the imbalance of the components. The eutectic composition of 63 percent tin and 37 percent lead is the most preferred. The additional bath components which are necessary in order to obtain a mirror bright solder deposit include formaldehyde, an aryl primary amine, a condensation product of an aromatic aldehyde and an aromatic amine, a polynuclear aromatic disulfonic acid or salt, and a surfactant combination.

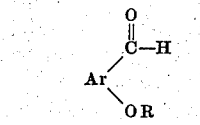
DETAILED DESCRIPTION OF THE INVENTION

Formaldehyde should be present in the composition in an amount between 6 and 12 grams per liter, preferably in an amount between 8 and 10 grams per liter. It is conveniently added as formalin, a 37 percent aqueous solution of formaldehyde. The aryl primary amine should be present in an amount of at least 0.1 grams per liter, preferably between 0.1 and 0.9 grams per liter, and most preferably between 0.3 and 0.6 grams per liter. Amines suitable for this purpose may be represented by the following formula:

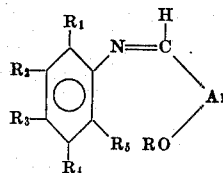


wherein R_1 through R_5 are independently selected from the group of substituents consisting of alkyl and alkoxy groups having up to four carbon atoms, halide and hydroxy. The most preferred compound having this structure is o-anisidine.

The aromatic aldehyde has the following structural formula:

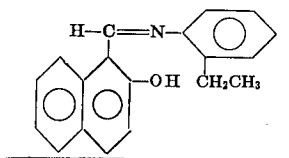


wherein R is selected from a group consisting of alkyl and hydrogen; Ar is an aryl radical having up to 2 fused rings substituted or not with alkyl or alkoxy groups having up to 4 carbon atoms or halide; and wherein the two substituents of the above formula are ortho to each other. The condensation product therefore may be represented by the general formula:



It has been found that the condensation product of 2-hydroxy naphthalene-1-carboxaldehyde and o-ethylaniline is the preferred compound of this type since it minimizes the amount of formaldehyde required in the electrolytic solution. This bath component should be present in an amount of from 0.001 grams per liter up to the solubility limits of the solution. Normally, the concentration will be between 0.01 and 0.1 grams per liter. The product of the above-

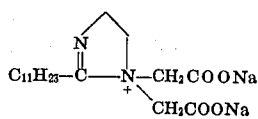
mentioned condensation reaction has the following structural formula:



Methods for the preparation of such condensation products may be found in *Chemistry of the Carbon-Nitrogen Double Bond*, Sol Patai, Editor, Inter Science (1970), or in similar books on organic-nitrogen chemistry.

The polynuclear aromatic disulfonic acid component must have at least two fused aromatic rings and two sulfonic acid or sulfonate substituents. In the case of the naphthalene derivative, naphthalene-2,7 disulfonic acid disodium salt is preferred. While only a very small amount of this component is necessary in order to obtain a bright deposit, if it is omitted inferior results are obtained. Amounts ranging from less than 0.001 grams per liter up to 0.02 grams per liter are sufficient while amounts between 0.001 and 0.005 grams per liter are preferred.

The surfactant combination necessary to obtain a bright solder deposit must include an anionic surfactant, a nonionic surfactant, as well as an amphoteric surfactant. Suitable anionic and amphoteric surface active agents may be selected from any of those found in handbooks on the subject. A preferred anionic surfactant is Aerosol 22, trademark for a product manufactured by the American Cyanimid Company, and comprising a 35 percent active solution of tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl-sulfosuccinamate. Preferred amphoteric surfactants include Miranol HM a substituted imidazoline having the approximate formula:



manufactured by the Miranol Chemical Company, and Triton QS-15 manufactured by Rohm & Haas Company which contains the sodium salt of a sulfonated tertiary amine. Of the non-ionic surfactants, the only one found effective is Luprintol P manufactured by BASF-Wyandotte which is a polyethoxylated benzyl phenol. The surfactants may be present in trace amounts or more.

Excess quantities of surfactants are not desirable because they provide no further improvement in the resulting solder plate. Optimum results can normally be obtained with concentrations of each of these types of surfactants of less than 1 gram per liter. Suitable plating conditions are those conventional in the art, for example, as disclosed in the aforementioned U.S. patent. Typically, the temperature of the plating bath will be about room temperature or below and the current density will be at least 12 A.S.F., preferably less than 50 A.S.F., and most preferably about 30 A.S.F. Additional

additives may be included in the bath for varying purposes. Boric acid may be used to stabilize the free fluoboric acid in the bath, and other materials such as alkanols may be included to inhibit attack by the composition upon portions of the workpiece which are susceptible to degradation such as resist layers.

Best plating results are obtained from the solution is agitated although vigorous agitation is not required. It has also been found very helpful to maintain the current ripple at a value of less than 5 percent.

EXAMPLES

In each experiment, the organics were added to a standard bath containing about 2 oz/gal (15 g/l) tin as the divalent cation, 1 1/2 oz/gal (10 g/l) lead as the divalent cation, 23 oz/gal (172.5 g/l) fluoboric acid and 2 oz/gal (15 g/l) boric acid. The pH of such a solution is below 1. The tin and lead were added as the fluoborates to avoid introduction of interfering anions.

Test panels were steel having a polished copper plate of approximately 50 millionths of an inch thick. Test circuit boards were copper-plated and covered with a resist except for 8 parallel lines having thru-holes at each end thereof.

HNCEA is a shorthand notation for the condensation product of 2-hydroxy naphthalene-1-carboxaldehyde with o-ethylaniline and NDAS is shorthand for naphthalene-2,7 disulfonic acid disodium salt.

The following were added to the standard bath:

| Component | g./l. |
|---|-------|
| Formaldehyde | 9.0 |
| o-anisidine | 0.45 |
| HNCEA | .0045 |
| NDAS | .005 |
| Non-ionic Surfactant β naphthol + 13 ethylene oxide | .035 |
| Luprintol P | 0.35 |
| Anionic surfactant | |
| Aerosol 22 | 0.27 |
| Amphoteric surfactant | |
| Triton QS-15 | 0.2 |

Test panels and circuit boards were plated at 30 A.S.F. for 10 minutes at room temperature using one bagged anode, a rectifier with 5 percent ripple or less and with rocker arm agitation. The solder deposit was mirror bright and exhibited a slight haze. Similar tests without NDAS yielded solder deposits having a much more noticeable haze. When melted, the solder exhibits excellent adherence.

Additional experiments were performed varying the concentration of the ingredients. Deposit quality was found to be noticeably superior when the concentrations were within the ranges specified in the foregoing description.

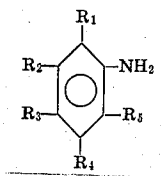
What is claimed is:

1. An aqueous acidic composition suitable for electroplating a bright tin-lead alloy of high solderability, comprising:

a. 3.5 - 60 g/l divalent tin;

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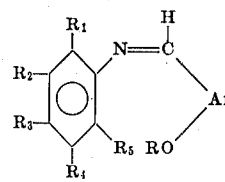
- b. 30 - 45 wt. percent divalent lead, based on the total of lead and tin in the bath;
 c. 6-12 g/l formaldehyde;
 d. at least 0.1 g/l of an aryl primary amine;
 e. at least 0.001 g/l of a condensation product of an aromatic aldehyde and an aromatic amine; and
 f. a surfactant combination comprising:
 1. an anionic surfactant;
 2. an amphoteric surfactant; and
 3. a non-ionic surfactant.
2. The composition of claim 1 additionally comprising at least 0.001 g/l of a polynuclear aromatic disulfonic acid or salt thereof.
3. The composition of claim 2 wherein said sulfonic acid comprises at least two fused aromatic rings and two sulfonic acid substituents, said rings substituted or not with alkyl or alkoxy groups of up to four carbon atoms or a halide.
4. The composition of claim 1 wherein said aryl primary amine has the formula:



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wherein R_1 through R_5 are independently selected from the group of substituents consisting of alkyl and alkoxy groups having up to four carbon atoms, halide and hydroxy.

5. The composition of claim 4 wherein said condensation product is represented by the formula:



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15 wherein R_1 through R_5 are independently selected from the group consisting of alkyl and alkoxy groups of up to four carbon atoms, hydroxy, halide and hydrogen; R is selected from the group consisting of alkyl and hydrogen, Ar is an aryl radical having up to two fused rings, substituted or not with halide, alkyl or alkoxy groups having one to four carbon atoms.

6. A method of electroplating solder on a base metal surface comprising electrolyzing the composition of claim 1 with said base metal as cathode.

25 7. The method of claim 6 wherein said composition additionally comprises at least 0.001 g/l of a polynuclear aromatic disulfonic acid.

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