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3,791,941 GOLD PLATING BATH FOR BARREL PLATING OPERATIONS

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No Drawing. Continuation-in-part of applications Ser. No. 273,860, July 21, 1972, and Ser. No. 288,020, Sept. 11, 1972. This application Oct. 13, 1972, Ser. No. 297,288

Int. Cl. C23b 5/28

U.S. Cl. 204—46

14 Claims

ABSTRACT OF THE DISCLOSURE

An electroplating bath particularly suited for barrel plating operations. The bath includes in addition to an alkali-gold cyanide, a bath soluble salt of N,N-di-2-hydroxyethylglycine or of glycine, or glycine itself may be utilized. The bath further includes quantities of hydrazine, small amounts of arsenic and/or lead ion, and a buffering agent such as phosphate ion.

This application is a continuation-in-part of our co-pending applications: Ser. No. 273,860, filed July 21, 1972, for "Gold Plating Bath for Barrel Plating Operations"; and Ser. No. 288,020, filed Sept. 11, 1972, for "Gold Plating Bath for Barrel Plating Operations." Each of the said applications is assigned to the same assignee as the instant application.

BACKGROUND OF INVENTION

This invention relates generally to electroplating baths, and more specifically relates to such baths as are useful in barrel gold plating operations.

Gold, within recent years, has become a very important part of the electronics industry. Among those properties recommending its use are its relative inalterability, high solderability, and low contact resistance. In the semiconductor field, gold has furthermore found favor because of its ability to readily form a eutectic alloy with silicon and germanium.

In the latter connection, it may be noted that most headers or packages for diodes, transistors, and integrated circuits are gold plated as a preparation for the mounting or attaching of the semi-conductor devices. For such an application, the gold deposit must be of high purity and deposited as uniformly as possible, in order to readily alloy with silicon or other metallic contacts. The problem of plating such parts is compounded by the fact that these components are irregularly shaped and of complicated design. Such parts are exemplified by the well-known line of TO-5 and TO-8 multi-lead headers. Such headers consist of an eyelet of Kovar metal to which several insulated Kovar leads are attached and sealed in glass.

In accordance with known principles in the art, headers of the foregoing type have in the past been plated (among other methods) by so-called barrel plating techniques—that is, by subjecting such articles to electroplating while a plurality of articles tumble in a barrel. When such articles are thus plated, however, it is found that many leads do not make electrical contact with the remainder of the load. Where such condition obtains during the plating cycle, the portion of the lead closest to the anode becomes cathodic. Such leads become bipolar, and at the anodic portions of the leads problems can arise in that (a) the gold may redissolve anodically; and (b) the base metal can be attached to expose bare spots. Should the tumbling action be markedly inadequate, these problems can become quite severe. In the past these problems have partially been overcome by incorporating mechanical means

for improving the electrical conductivity through the load. Such means have taken the form of metal particles or metal shot. Unfortunately, during the plating operation, the shot itself becomes gold-plated, resulting in loss of gold and attendant increase in the cost of plating the desired objects—i.e. the headers, etc.

In our above-cited co-pending application Ser. No. 273,860, we have disclosed our finding that an alkali-gold cyanide electroplating bath including a chelating phosphonic acid, with additional quantities of hydrazine and small amounts of arsenic and/or lead ion, eliminates or minimizes many of the cited problems, and in fact provides superior performance in the aforementioned barrel plating operations. The said baths, however, are in at least one important commercial respect less than satisfactory: we refer to the fact that the phosphonic acid compounds identified therein are relatively expensive, which tends to inhibit the otherwise advantageous use thereof.

In the above connection it is pointed out that it is known (see for example U.S. Pat. No. 3,551,305) that certain salts of the chelating amino acids, such as, for example, salts of N,N-di-2-hydroxyethyl-glycine are useful chelating agents for gold plating operations. These compounds, furthermore, in comparison particularly to the phosphonic acid compounds mentioned above, are relatively inexpensive. Unfortunately, however, the use of these compounds has, in the past, been sharply limited by the fact that they lack stability under anodic oxidation. In consequence of this, decomposition products have tended in the past to form in gold plating baths in which such materials are employed, with resultant contamination of the bath, or of the deposit. In order to rectify such condition it has, in the past, been required to regularly remove the decomposition products, as, for example, by means of activating charcoal, or the like. This phenomenon in turn has compounded the operating procedures and produced attendant cost and loss of operating time.

In accordance with the foregoing it may be regarded as an object of the present invention to provide electroplating bath compositions for use in barrel plating operations, which are highly effective in reducing effects of bipolarity.

It is a further object of the invention, to provide gold electroplating baths, for use in the barrel plating of electronic components or the like, which baths display reduced tendencies to attack the base metal of the said components.

It is another object of the invention, to provide gold electroplating baths, especially suited for use in barrel plating of electronic components or the like, which prevent or slow down co-deposition with the gold of the troublesome common impurities such as copper, nickel, cobalt, iron and lead.

It is a further object of the invention to provide gold electroplating baths enabling improved metal distribution and superior aesthetic properties in the resultant platings.

It is a still further object of the invention to provide gold electroplating baths which incorporate relatively inexpensive chelating agents, and which incorporate additional agents which act to prevent the formation of undesirable decomposition of products in consequence of anodic oxidation.

SUMMARY OF INVENTION

Now in accordance with the present invention, it has unexpectedly been discovered that the foregoing and other objects are achieved in an electroplating bath which includes in addition to an alkali-gold cyanide, a bath soluble salt of N,N-di-2-hydroxyethylglycine or of glycine together with quantities of hydrazine and small amounts of arsenic and/or lead ion. Glycine itself (amino-acetic acid)

may also be used instead of or in addition to the said salts. Phosphate ion is preferably present as a buffer; alternatively or in addition, other buffering agents may be utilized. The said combination in addition to eliminating or minimizing many of the cited problems previously found to exist during barrel plating operations, also (by virtue of its use of the cited chelating agents) enables formulations at relatively low cost. The cited chelating agents appear to function in the present environment to reduce the tendency of the compositions to attack the base metal, and by virtue of their chelating characteristics slow down or prevent co-deposition with the gold of the common impurities, such as copper, cobalt, nickel, iron and lead.

The electrolyte is kept slightly on the reducing side by the addition of the reducing agent, hydrazine. Such agent appears in the combination of the invention to greatly reduce or even eliminate the aforementioned tendency to anodic deplating of the parts being processed. Furthermore, for reasons that are not completely understood, the hydrazine, in the present composition acts to improve the throwing power of the bath. Additionally, a synergistic effect appears to occur in the present bath between the chelating agent and hydrazine, which acts to stabilize the present bath, well beyond that which might be anticipated on the basis of the individual components. One of the consequences of such synergistic effect appears to be a marked reduction in the tendency of the chelating agents to anodically oxidize. As a result decomposition products are maintained at minimal levels.

The trivalent arsenic ion and/or lead ion serve in the present environment to augment the smoothness of the deposit, yielding platings of superior aesthetic qualities, such as with respect to lustre and color thereof. The addition of as little as 1.5 mg. of As^{+++} or 2 mg. of Pb^{++} per liter of solution, refines the grain of the deposit and provides an attractive pale yellow semi-bright gold deposit of attractive lemon-yellow color and of low porosity. For reasons that are not completely understood these additives appear in the environment of barrel plating operation, to greatly improve the resulting metal distribution.

DESCRIPTION OF PREFERRED EMBODIMENT

Among the chelating agents which may be utilized in the baths of the present invention are the bath soluble salts of N,N-di-2-hydroxyethylglycine (DHG, and of glycine (amino-acetic acid), as well as glycine itself. A preferred compound of this type for use in the invention, is sodium dihydroxyethyl glycinate, available from Geigy Industrial Chemicals under the trade name "Chel 185." A similar compound is also available from the Cowles Chemical Division of Stauffer Chemicals under the trade-name "Chelon DHG." The cited chelating agents are present in the baths of the present invention in a preferred concentration range of from 50 to 250 g./l. The compounds cited exhibit high stability constants, in particular exhibiting relatively high pK values with respect to chelated metallic impurities, such as for example, copper, nickel, cobalt, iron, etc.

EXAMPLES 1-4

A series of four gold electroplating baths were prepared in accordance with the present invention, incorporating the following components (where "DHG" refers to sodium dihydroxyethyl glycinate):

Bath	1	2	3	4
DHG, ml./l.	150	100	100	100
Hydrazine, 64%, ml./l.	5	20	15	10
Au, g./l.	8	8	3	2
As^{+++} , mg./l.	4	2	2	2
Potassium phosphate monobasic, g./l.	150	100	150	100
Boric acid, g./l.		70		
pH	7.0	7.0	4.5	4.3

All of the baths cited above were operated at 50° C. and at current densities of 5 a.s.f., and were found to be highly suitable for barrel plating of parts such as the

cited TO-5 headers. Baths 2, 3 and 4 were found to be relatively unstable on standing; baths 3 and 4 broke down after three (3) days. Bath 2 was of superior stability, breaking down after a week.

Example V

A preferred bath in accordance with the invention, was prepared as follows:

Potassium phosphate monobasic	g./l.	100
Boric acid	g./l.	60
DHG	ml./l.	150
Hydrazine 64%	ml./l.	10
As^{+++}	mg./l.	4
Au	g./l.	8
pH adjusted by small quantities of KOH or NaOH to 7.0.		

Very satisfactory gold deposits were obtained from this bath, which was found to be very stable in production. In this example the potassium phosphate monobasic and boric acid serve as buffers. In general, it is preferable with the baths in the invention to adjust the pH with such buffers to about 7.0. Phosphoric acid may also be utilized for this purpose, as may other buffering systems based on borates or citrates. It may be noted that in the absence of buffers of these or similar types, relatively inferior deposits are obtained. This is likely due to the fact that the chelating agents specified are amino acids of the type known to form internal salts. The amino and carboxyl radicals of such acids saturate themselves intramolecularly just as an amine is neutralized externally by a carboxylic acid. Since DHG contains only one basic (NH_2) group and one carboxyl group, it reacts almost neutral. It appears therefore since the addition of acids are required to yield superior results, that some free or unneutralized acids must be present in the solution.

The As^{+++} ion is preferably present in minimum concentration of 1.5 to 2 mg./l. calculated as As^{+++} . In place of, or in addition to the As^{+++} ion, it has been found that small quantities of Pb^{++} ion may be utilized, with consequent marked improvement in the properties of the deposit—including refinement of grain, production of porosity, and better metal distribution. Resultant improvement of aesthetic qualities, such as lustre and color is similarly evidenced. Where lead is used alone as little as 2 mg./l. are thus effective (calculated as the metal), with the useful range of addition extending up to about 12 mg./l. The lead may be in the form of bath soluble salts, such as lead nitrate and lead acetate. It may be observed in connection with the present results that it is quite unexpected in view of the fact that lead ion acts as a most undesirable impurity in pure gold deposits plated from citrate or phosphate-citrate systems not including the other components of the present baths.

Example VI

A bath in accordance with the invention, was prepared as follows:

Glycine (amino-acetic acid)	g./l.	100
Hydrazine 64%	ml./l.	20
Phosphoric acid to pH to 7.0.		
As^{+++}	mg./l.	2
Au	g./l.	8

In this, as in the baths of the prior examples, KOH or NaOH can be utilized to adjust the pH to the desired level. Similarly the glycine may be replaced by the alkali metal salt such as sodium glycinate (available from Hampshire Chemical Division of W. R. Grace Co., Nashua, N.H.). This cited bath was utilized to plate a representative panel at 50° C. and at a current density of .5 ampere per square decimeter to yield a deposit of 80 micro-inch thickness of gold. The panel was then baked

at 500° C. for 5 minutes. The resultant plating was of good distribution and no discoloration developed.

The gold cited for use in all of the foregoing examples is calculated as the metal and is added to the compositions preferably as a standard 68% P.G.C. (potassium gold cyanide) solution. Other alkali-gold cyanide solutions, such as sodium, or ammonium gold cyanide solutions may be used. As metallic gold, the element may be present in the approximate range of from about 2 g./l. to saturation, with a practical upper limit being about 32 g./l. The hydrazine 64% (hydrazine hydrate) is a product available from Fairmount Chemical Co., Newark, N.J. The said hydrazine 64% may be present in the bath in the approximate range of from 5 ml./l. to 100 ml./l., or somewhat higher. In preparing the bath, the several components are added to the bath in the order indicated, with sufficient water being added to provide one liter of solution. The preferred concentration of hydrazine (calculated as 64% hydrazine) is about 10-20 ml./l. for typical applications, such as where headers like the TO-5 and TO-8 are plated. Concentrations substantially beyond this level yield little additional benefits.

The baths of the invention are typically used at a pH of about 7.0, with a preferred operating range being from about 6.0 to 8.0. Typical operating temperatures are from about 32° C. to 54° C., with a preferred operating range being from about 49° C. to 52° C. Maximum increased stability of baths in accordance with the invention are achieved in the pH range of 6.0 to 8.0. It will be appreciated by those skilled in the art that such result is unexpected as the reducing abilities of hydrazine would normally be anticipated to increase with increasing pH, especially in the alkaline range between 7.0 and 8.0.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art. The compositions set forth, for example, while being particularly adapted for use in barrel plating operations, also find application in other plating environments, as for example in rack or still plating operations, where it is chiefly the distribution of metal which is of concern. Accordingly the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

We claim:

1. An electroplating bath for barrel plating of gold, comprising an aqueous solution of an alkali-gold cyanide, said gold being present in concentrations of from about 2 g./l. to saturation calculated as the metal; for about 50 to 250 g./l. of a chelating agent selected from the group consisting of glycine and the bath soluble alkali metal salts of glycine and N,N-di-2-hydroxyethylglycine; from about 5 ml./l. to 100 ml./l. of hydrazine calculated as 64% hydrazine; and as an agent for improving the distribution and aesthetic qualities of the deposit, one or more agents selected from the group consisting of arsenic and lead ion, said ion being in sufficient quantity to provide a smoother and more evenly distributed deposit than is obtained in the absence thereof.

2. A composition according to claim 1, further including quantities of buffers, adequate to adjust the pH of said bath between 6.0 and 8.0.

3. A composition according to claim 2, wherein said ion agent is present in concentrations of less than about 12 mg./l.

4. A composition according to claim 3, wherein said ion agent comprises As^{+++} in a concentration range of from about 1.5 to 12 mg./l.

5. A composition according to claim 3, wherein said ion agent comprises Pb^{++} in a concentration range of from about 2 to 12 mg./l.

6. A composition according to claim 2, wherein said chelating agent comprises the sodium salt of N,N-di-2-hydroxyethylglycine.

7. A composition according to claim 2, wherein said chelating agent comprises sodium glycinate.

8. A composition according to claim 2, wherein said chelating agent comprises glycine.

9. A composition according to claim 2, wherein said buffers include phosphate ion.

10. A method for improved electroplating of complex-shaped metallic articles comprising: subjecting said article to electroplating in a barrel-type operation utilizing as an electroplating bath an aqueous solution of an alkali gold cyanide, said gold being in concentrations of from about 2 g./l. to saturation calculated as the metal; from about 50 to 250 g./l. of a dissolved chelating agent selected from the group consisting of glycine and the bath soluble alkali metal salts of glycine and N,N-di-2-hydroxyethylglycine; as an agent for reducing bipolarity effects, from about 5 ml./l. to 100 ml./l. of hydrazine calculated as 64% hydrazine; and as an agent for improving the distribution and aesthetic qualities of the deposit, less than 12 mg./l. of an ionic agent selected from the group consisting of arsenic and lead ion, said ion being in sufficient quantity to provide a smoother and more evenly distributed deposit than is obtained in the absence thereof.

11. A method according to claim 5, wherein the pH of said bath is maintained between about 6.0 and 8.0.

12. A method in accordance with claim 11, wherein said plating operation is conducted at temperatures of from about 49° to 52° C.

13. A method in accordance with claim 11, wherein said ion agent comprises As^{+++} in the concentration range of from about 1.5 to 12 mg./l.

14. A method in accordance with claim 11, wherein said ion agent comprises Pb^{++} in a concentration range of from about 2 to 12 mg./l.

References Cited

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U.S. Cl. X.R.

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