

[54] **GOLD PLATING BATH FOR BARREL PLATING OPERATIONS**

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[57] **ABSTRACT**

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[58] Field of Search..... **204/46, 43 G, 109; 106/1; 117/130 E**

An alkali gold cyanide bath particularly suited for barrel plating operations. The bath includes a chelating phosphonic acid, with quantities of hydrazine and small amounts of arsenic and/or lead ion. Bipolarity effects in plated objects are minimized through use of the composition. The bath displays reduced tendencies to attack the base metal of objects being plated or to codeposit undesired metals with the gold. Improved distribution of deposited metal is enabled with the resultant plating having excellent aesthetic qualities, and superior bake-out characteristics.

[56] **References Cited**

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14 Claims, No Drawings

GOLD PLATING BATH FOR BARREL PLATING OPERATIONS

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 semi-conductor 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 the 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 become 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 attacked to expose bare spots — especially where the plating solution includes high concentrations of citrates or phosphates. Should the tumbling action be markedly inadequate, 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 become gold-plated, resulting in loss of gold and attendant increase in the cost of plating the desired objects — i.e., the headers or so forth.

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 the 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 display reduced tendencies to attack the base metal of the said components.

It is another object of the invention, to provide gold electroplating baths, for use in barrel plating of electronic components or the like, which prevent or slow down codeposition with the gold of the troublesome

common impurities such as copper, nickel, cobalt, iron and lead.

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

SUMMARY OF INVENTION

Now, in accordance with the present invention, it has been found 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.

In accordance with the invention, the conductivity salts and buffers normally used in a gold plating solution, such as phosphates, citrates and the like, are replaced by an organic phosphorous compound, such as ethylenediamine tetra methylenephosphonic acid; 1, hydroxyethylidene 1, 1 diphosphonic acid, or aminotri (methylenephosphonic acid). The indicated compounds are available from the Monsanto Company of St. Louis, Missouri, under the product designations "Dequest 2041," "Dequest 2010," and "Dequest 2000," respectively. In the present compositions, these compounds appear to reduce the tendency of the compositions to attack the base metal, and by virtue of their chelating characteristics slow down or prevent codeposition with the gold of the common impurities such as copper, nickel, cobalt, iron and lead,

The organo-phosphorous compounds cited above are also useful in the present environment because of their unusual stability under anodic oxidation. This results in greater bath stability and purer deposits since no decomposition products contaminate the bath or the deposit. Furthermore, operating costs are reduced since addition of the organic phosphorous compounds are only required to compensate drag-out losses.

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. Furthermore, as will be discussed in greater detail hereinbelow, a synergistic effect occurs in the present bath between the chelating phosphonic acid and hydrazine, which acts to stabilize the present baths well beyond what might be anticipated on the basis of the individual components.

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 luster and color thereof. The addition of as little as 0.4 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 with 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

Example I

An electroplating bath was prepared in accordance with the invention, incorporating the following components:

	1 liter
ethylenediamine tetra methylenephosphonic acid	160 g
Potassium hydroxide	75 g
hydrazine 64%	25 ml
gold (as PGC)	8.2 g
As ⁺⁺⁺	0.8 mg

The several components are added to the bath in the order indicated, with sufficient water being added to provide 1 liter of solution. The chelating phosphonic acid specified (ETMA) is the previously referred-to commercial compound "Dequest 2041." This component is preferably present in the range of from about 80 grams to 320 g/l, corresponding to a specific gravity range of from about 8° Baume. The hydrazine 64 percent (hydrazine hydrate) is a product available from Fairmount Chemical Co., Newark, N. J. The said hydrazine 64 percent may be present in the bath in the approximate range of from 5 ml to 100 ml/l or somewhat higher.

Gold is added to the composition of Example I preferably as a standard 68 percent 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 gr to saturation, with a practical upper limit being about 32 g/l.

The As⁺⁺⁺ ion may be added in the form of numerous bath-soluble salts, as for example, as sodium or potassium arsenate. The concentration of As⁺⁺⁺, calculated as the metal, may usefully run from about 0.4 mg to 12 mg/l, with the best metal distribution in the resultant plated product occurring at a concentration of about 0.8 mg/l, to 2 mg/l.

In place of or in addition to the As⁺⁺⁺, 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, reduction of porosity and better metal distribution. Resultant improvement of aesthetic qualities, such as luster 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 added 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.

The below Example II illustrates the effects of component concentrations (all concentrations are in terms of per liter of solution):

Example II

	Bath 1	Bath 2	Bath 3
gold (as P.G.C.)	8 g	8 g	8 g
ETMA	80 g	160 g	320 g
potassium hydroxide	37.5 g	75 g	150 g
hydrazine 64%	13 ml	26 ml	52 ml
As ⁺⁺⁺	1 mg	1 mg	1 mg
pH adjusted to	7.0-7.3		7.0-7.3

temperature	50°C	50°C	50°C
approximate specific gravity at 25°C	8°B	60°B	2.97°B

As will be evident to one skilled in the art, Bath 2 above provides the best utilization characteristics because of its specific gravity of 16° Baume. Bath 3 is of limited interest because of its high specific gravity of 29.7° Baume, which renders it too viscous for most applications. Bath 1 is somewhat on the light side, although suitable for certain applications, such as strike, etc. A preferred specific gravity is about 16°B, and there is little advantage in baths above about 20°B for most applications.

The preferred concentration of hydrazine (calculated as 64 percent hydrazine) is about 25 ml per liter, for typical applications, such as where headers like the TO-5 and TO-8 are plated. Concentrations substantially beyond this level yield little additional benefit.

The action of the hydrazine in the present bath appears to be much more than that of a mere reducing agent. Rather, it appears that a synergistic action occurs by virtue of the combination of the chelating acid, such as the cited ethylenediamine tetra methylenephosphonic acid (ETMA), with the hydrazine. Thus is observed that the cited combination stabilizes the baths well beyond what might be anticipated in the absence of synergistic effects — since gold plating baths with large concentrations of hydrazine are normally destroyed during electrolysis. This aspect of the invention is illustrated by comparative data for two baths, (Examples III and IV) which baths utilize hydrazine, but differ with respect to the acid additive.

Example III

A bath was prepared as follows:
 gold (as P.G.C.) — 8 g/l
 monosodium phosphate — 50 g/l
 citric acid — 110 g/l
 hydrazine 64 percent — 100 ml/l
 As⁺⁺⁺ — 2 mg/l
 pH adjusted to — 7.0
 temperature — 50°C

A panel was plated at 0.4 amp per square decimeter in the above solution and was acceptable with a pleasing lemon-yellow color. The efficiency was found to be 127.6 mg per ampere-minute (which indicates an electroless action since the maximum efficiency for a gold plating solution is 122.6 mg per ampere-minute). The said bath was stable overnight, but after a few days of standing at room temperature the bath broke down and the gold started to precipitate out.

EXAMPLE IV

A bath was prepared as follows:
 gold (as P.G.C.) — 8 g/l
 ETMA — 160 g/l
 hydrazine (64 percent) — 100 ml/l
 As⁺⁺⁺ — 2 mg/l
 Ph adjusted to — 7.0
 temperature — 50°

A panel was plated in the above solution at 0.4 amp/dm² and was deemed acceptable with a pleasing and smooth lemon-yellow color. The efficiency was found to be 128.8 mg per ampere-minute. The bath, in contrast to that of Example III, was stable and continued to be stable for several weeks.

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. This point is well illustrated by the following Example of the lower pH bath:

EXAMPLE V

A bath was prepared as follows:
 gold (as P.G.C.) — 3 g/l
 ETMA — 160 g/l
 hydrazine 64 percent — 25 ml/l
 potassium hydroxide — 30 g/l
 As⁺⁺⁺ — 2 mg/l
 pH adjusted to — 4.2
 temperature — 45°C

The indicated bath is very useful and is the preferred strike bath to precoat TO-5 and TO-8 multilead headers, by virtue of its pH of 4.3 — which is necessary to provide good adhesion on Kovar and similar related alloys. The bath at pH of 6 to 8 does not normally provide good adhesion over Kovar and other ferrous alloys. The efficiency of the Example V bath is about 122 mg per amp-minute at 45°C and with current densities of 0.4 amp/dm² (still plating). The stability of the bath at pH of 4.3 is much less than that of the preferred bath at pH of 6.0 to 8.0. In particular the gold slowly plates out on the side of the tank heaters, anodes, etc. The bath performs satisfactorily provided the gold content is maintained above about 2 g/l — with the other components being in the range otherwise specified for the invention. However, the bath has a much shorter life and must be changed more often, in contrast to which the baths having pH's of about 6.0 to 8.0 and temperatures of about 50°C, have unlimited life and need be changed only when the level of contaminants (especially organics) becomes excessive.

The combination of hydrazine and the phosphonic acid such as the cited ETMA compound, also appears to provide much stronger chelates with the metallic impurities such as nickel, cobalt, etc. By the said combination, the already strong tendency of the cited phosphonic acid compounds to prevent codisposition of the said impurities, is thus augmented.

The baths of the invention are typically used at a pH of about 7.3. Good results are achieved with pH's as low as 4.0, but a preferred operating range is from about 6.0 to 8.0. Typical operating temperatures are from about 90°F to 130°F, with a preferred operating range being from about 120° to 125°F.

Samples prepared from plating baths as in the foregoing Examples are found to possess excellent smoothness, luster, uniformity and color, and are found to be markedly free from the common barrel plating defects heretofore discussed. The platings, moreover exhibit improved quality after bake-out, as compared to platings of the prior art.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant teaching, 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 that 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 alkali gold cyanide, said gold being in concentrations of from about 2 g/l to saturation calculated as the metal; from 80 to 320 g/l of a dissolved chelating phosphonic acid; as a reducing agent and for improving the throwing power of said bath, from about 5 ml to 100 ml/l of hydrazine calculated as 64 percent 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 a soluble alkali-metal base adequate to adjust the pH of said bath to between 4.0 and 8.0.
3. A composition according to claim 2, wherein the pH of said composition is maintained at between 6.0 and 8.0.
4. A composition according to claim 3, wherein said phosphonic acid comprises ethylenediamine tetramethylenephosphonic acid.
5. A composition according to claim 4 wherein said ion agent is present in concentrations of less than about 12 mg/l.
6. A composition according to claim 5, wherein said ion comprises As⁺⁺⁺ in a concentration range of from 0.4 to 12 mg/l.
7. A composition according to claim 5, wherein said ion comprises Pb⁺⁺ in a concentration range of from about 2 to 12 mg/l.
8. An electroplating bath for barrel plating of gold, comprising per liter of aqueous solution about 160 g ethylenediamine tetra methylenephosphonic acid; as a reducing agent and agent for improving bath throwing power, about 25 ml of hydrazine, calculated as 64 percent hydrazine; potassium gold cyanide in concentrations to provide about 8.2 g of gold, calculated as the metal; and as an agent for improving the distribution and aesthetic qualities of the deposit about 0.8 mg of arsenic ion; together with sufficient alkali-metal hydroxide to yield a pH of about 7.3.
9. A method for improved electroplating of complex-shaped metallic articles comprising: subjecting said articles to electroplating in a barrel-type operation utilizing as an electroplating bath an aqueous solution of alkali gold cyanide, said gold being in concentrations of from about 2g/l to saturation; from 80 to 320 g/l of a dissolved chelating phosphonic acid; as an agent for reducing bipolarity effects, from about 5 ml to 100 ml/l of hydrazine calculated as 64 percent 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.
10. A method in accordance with claim 9, wherein said ion is present in concentrations of less than about 12 mg/l.

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11. A method in accordance with claim 10, wherein said plating operation is conducted at temperatures of from about 120° to 125°F.

12. A method in accordance with claim 10, wherein said ion comprises As⁺⁺⁺ in the concentration range of from about 0.4 to 12 mg/l.

13. A method in accordance with claim 10, wherein

said ion comprises Pb⁺⁺ in a concentration range of from about 2 to 12 mg/l.

14. A method according to claim 9, wherein said phosphonic acid comprises ethylenediamine tetra methylenephosphonic acid.

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