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[54] **BRIGHT GOLD ELECTROPLATING BATH AND METHOD OF ELECTROPLATING BRIGHT GOLD**

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[63] Continuation-in-part of Ser. No. 176,263, Aug. 20, 1971, abandoned.

[52] **U.S. Cl.** ..... **204/43 G,** 204/46 G

[51] **Int. Cl.** **C23b 5/28,** C23b 5/42, C23b 5/46

[58] **Field of Search** ..... 204/43 G, 46, 44

[56] **References Cited**

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[57] **ABSTRACT**

A bright gold electroplating bath comprising: an aqueous solution of an alkali metal gold cyanide; as an alloying agent, cobalt or nickel, in the form of a complex with at least aminoguanidine and a chelating phosphonic acid; and as conducting and buffering agents, one or more bath soluble phosphates.

10 Claims, No Drawings

BRIGHT GOLD ELECTROPLATING BATH AND METHOD OF ELECTROPLATING BRIGHT GOLD

This application is a continuation-in-part of our co-pending application, Ser. No. 176,263, filed Aug. 20, 1971, and now abandoned for "GOLD AND GOLD ALLOYS ELECTROPLATING BATH," which application is assigned to the same assignee as is the instant application.

BACKGROUND OF THE INVENTION

This invention relates generally to electroplating compositions and methodology, and more specifically relates to compositions and methods useful in the electroplating of bright gold.

Within recent years an increasing demand for high quality bright gold plating, e.g. for decorative and electronic applications, has prompted considerable industrial activity directed toward development of electroplating baths useful for such purposes. Significant contributions to the art of electroplating bright gold alloys are thus, for example, disclosed in U.S. Pat. Nos. 2,812,200 and 2,905,601. The first of these patents to F. Volk, discloses a phosphate-based bath operating in the substantially neutral pH range of 6.5 to 7.5. The alloying metal or metals in this bath are introduced into the composition in the form of double cyanides, such as sodium copper cyanide or potassium nickel cyanide. The said baths, which produce bright, aesthetically pleasing deposits, have been of significant value, particularly in countries such as Switzerland and Germany, where the production of thick, low carat, gold deposits in the 5 to 20 micron range, are much in demand, especially for the watch industry; and the baths are still widely used today for such applications. A principal disadvantage, however, of such baths are their requirement for relatively high plating temperatures (60° to 75°C) and their rather short life. In the latter respect it may be observed that such baths require changing upon the initial gold content being turned over four or five times.

Yet, a further disadvantage of these conventional phosphate-based baths is a tendency thereof to produce pitting in the resulting plating. Although the reason for this is not completely understood, it is hypothesized that undesirably high surface tension effects bubbling, and so forth, during the deposition process, which may induce the specified defects.

The cited, and more recent, U.S. Pat. No. 2,905,601 to Rinker et al, discloses the use of weak stable organic acids, principally citric acid, in alkali metal cyanide baths, employing cobalt, nickel, and indium as brighteners, the said baths being maintained in the pH range of 3 to 5. A principal advantage of these latter baths is one of providing a stable electrolyte with a long life, which yields good, bright deposits.

A principal teaching of the Rinker bath is the use of citric acid or other weak organic acids in alloy gold plating baths. It appears here that the citric acid, or other weak organic acid, acts in the acid gold electroplating baths, as to tend to slow down the rate of deposit of such metals as nickel, copper, and cobalt. A teaching of similar nature is also set forth in an earlier patent, namely, U.S. Pat. No. 1,924,439 to H. Kersten. However, a serious deficiency of the said baths is that the resulting deposits are often highly stressed, and as a practical matter are often limited for such reason to

thicknesses below about 5 microns. This detrimental effect probably is caused (at least in part) by hydrogen embrittlement and from the presence of organic decomposition products in the bath. It may be noted in the latter connection, that in such baths the rate of consumption of citric acid is about equal to the weight of gold deposited.

In principle, it would appear that a bright gold electroplating bath possessing the advantages set forth with respect to the phosphate-based formulations of Volk, and the stability achieved in the Rinker formulations, would be much desired — were the cited undesirable features of the said baths not present. Up to the present time, however, a bath satisfying such criteria has not been in evidence.

In accordance with the foregoing, it may be regarded as an object of the present invention, to provide electroplating baths useful in the plating of bright gold, which, while utilizing phosphates therein, possess a high degree of stability.

It is a further object of the present invention, to provide electroplating baths and methodology useful in the plating of bright gold, which are capable of yielding smooth, lustrous, high quality plating, even in thicknesses exceeding 5 microns.

It is a yet further object of the present invention, to provide electroplating baths useful in the plating of bright gold, which, while possessing the stability of citrate-based baths, do not require constant addition of salts to maintain bath conductivity and workability, as is characteristic of the citrate baths; and which furthermore yield the comparatively brighter deposits that are characteristic of phosphate-based baths.

SUMMARY OF THE INVENTION

Now in accordance with the present invention, the foregoing objects, and others as will become apparent in the course of the ensuing specification, are achieved in a phosphate-based bright gold electroplating bath, wherein the cobalt or nickel is present in the form of a complex of specified phosphonic acids with aminoguanidine. By incorporating the base metal in the indicated complex form, the prior art disadvantages of the phosphate baths are overcome, in consequence of which the baths of the invention exhibit excellent stability and yield high quality platings, devoid of pitting, surface irregularities or the like, and possessing low porosity, and good grain and color, even in platings of relatively high thickness. The additive aminoquanidine appears to function somewhat in the present environment in an analogous way to the function of the weak organic acids in the cited U.S. Pat. Nos. 1,924,439 and 2,905,601. In some manner, not completely understood at the present time, a synergistic action appears to occur between the phosphonic acids of the invention and aminoguanidine, with the action of the resultant combination being such as to in part enable the results achieved in the invention.

Phosphates are present in the baths as the ammonium or alkali metal salts, and serve as conducting and buffering agents. In preparing the baths of the invention one adds the conducting and buffering compounds in quantities which yield a bath specific gravity appropriate to the bath application. Thereupon the pH of the bath, as required, may be adjusted by addition of small quantities of innocuous acids or bases — as is known in the art. A useful specific gravity range for the baths

is between about 6° to 20° Baume, and a preferred range between about 10° and 16° Baume.

The aminoguanidine, which is initially added in the form of the bicarbonate ($CH_6N_4.H_2CO_3$), available e.g. from Eastman Organic Chemicals of Rochester, New York, is typically present in the bath in concentrations of from about 2 to 50 g/l, and preferably in the range of about 5 to 35 g/l, calculated as the bicarbonate. Gold may be present in the baths in concentrations of from about 2 g/l to saturation. The alloying cobalt and/or nickel is typically present in concentrations of from about 5 mg/l to about 40 g/l, calculated as the metal, with a preferred level being between about 10 mg/l and 5 g/l, calculated as the metal.

DESCRIPTION OF PREFERRED EMBODIMENT

In order to illustrate the advantages of the unique combination of the present invention, an electroplating bath is firstly set forth in Example I below, which is basically a prior art phosphate-based bath; and in Example II a bath is set forth utilizing a combination resembling in some respects the baths of the present invention, but devoid of the aminoguanidine which is present (in a complex) in the baths of the invention:

Example I

Monopotassium phosphate	80 g/l
cobalt, as cobalt sulfate	50 mg/l
Gold, as potassium gold cyanide	8 g/l
pH adjusted to	4.3
Plating temperature	35°C

Example II

Mono ammonium phosphate	150 g/l
Cobalt, as complex with amino-trimethylenephosphonic acid	1 g/l
Gold, as potassium gold cyanide	8 g/l
pH adjusted to	4.3
Plating temperature	35°C

In each instance in the above, the cobalt and gold are calculated as the metal. Test panels prepared by electroplating from each of the baths of Examples I and II displayed a bright deposit, which, however, was not uniform in color. Some areas of the said panels were richer in gold coloration than other areas, it appearing that the gold tended to deposit in strongly agitated areas.

For purposes of the ensuing Examples, a cobalt complex was prepared as follows:

Example III

Amino trimethylenephosphonic acid (ATMPA)	140 ml
Aminoguanidine bicarbonate	50 g
Cobalt carbonate (45.1% cobalt metal)	44 g
Deionized water to yield	1000 ml

In a typical procedure for preparing the said cobalt complex, the cited phosphonic acid (which is available commercially from Monsanto under the designation "Dequest 2000") is diluted, and the cobalt carbonate slowly added. Thereupon the resulting mixture is warmed to completely dissolve the cobalt carbonate. The aminoguanidine carbonate is thereafter added very slowly, the resulting admixture filtered, if necessary, and the resultant pH adjusted to about 3.6 (typically from about 3.0 to 4.0). Each mililiter of the resultant concentrate contains approximately 20 mg of cobalt metal.

The corresponding nickel-based complex is prepared in accordance with the following composition:

Example IV

Ethylenediamine tetra methylene phosphonic acid (EDMPA)	200 grams
Nickel carbonate (48.5% nickel metal)	41.2 grams
Aminoguanidine	50 grams
Deionized water to yield	1000 ml

In a typical preparation procedure the phosphonic acid compound is agitated with the water to form an aqueous slurry, and the mixture warmed to 60° – 70°C. Thereupon the nickel carbonate is slowly added and agitation and heat are continued until the carbonate is dissolved, then the pH is adjusted, if necessary, with EDMPA or aminoguanidine to 3.0 to 5.0. As appropriate, filtering is then effected. Each ml of this solution contains approximately 20 mg of nickel as the metal.

EXAMPLE V

For purposes of this Example, the same bath as indicated in connection with Example II is utilized, except that in this instance the cobalt complex with aminoguanidine which is set forth in Example III was employed. More specifically 10 g/l of aminoguanidine was now present in the said electroplating bath. Coloration of the bath, in consequence, was completely distinct from that of Example II, indicating that a change had occurred in the complex used in Example II. Utilizing the bath of the present Example, panels plated under the substantially the same conditions as in Example II, were found to yield highly acceptable deposits superior in all respects to those of Examples I and II, but with the most marked improvement being in the uniformity of the resulting plating.

The phosphonic acid compound noted above, is one of a group of chelating phosphonic acids that are generally suitable for the present applications. The compound indicated, which may for purposes of convenience be referred to as ATMPA, is the preferable agent for use where cobalt is to be alloyed with the gold. The cited compound is not as effective where nickel is to be plated with gold, as is another well-known of the said chelating phosphonic acids, namely, ethylenediamine tetra methylene phosphonic acid (EDMPA). This latter compound is also available from Monsanto, under the designation "Dequest 2041." In preparing the complexes of Examples III and IV, the chelating phosphonic acid is added on approximately a 1:1 mole ratio with the nickel or cobalt — although an excess of the chelating agent is not objectionable.

The stability of the baths in acccordance with the invention can be increased further by the addition of from about 1 to 50 g/l of boric acid (preferably from about 10 to 30g/l) and from about 1 to 30 g/l of glycerine, as is described in British Pat. No. 1,218,732. In some instances the baths of the present invention still have a tendency to produce the insoluble compounds which occur where baths of the type set forth in Example I are utilized, such compounds being detrimental to the good performance of the bath. Consequently, pre-

ferred baths for use in accordance with the invention are set forth in Examples VI through IX below:

Example VI

Gold metal (P.G.C.)	8 g/l
Ammonium phosphate monobasic	150 g/l
Cobalt, as the complex of Example III	20 g/l
Boric acid	20 g/l
Glycerine	10 ml/l
pH (adjusted by NH_4OH or H_3PO_4 to)	3.8 to 4.9
Deionized water to make	1000 ml

The bath of the above Example VI operates very effectively at 37°C, and a current density up to 1.2 amp/dm². The ammonium salts used in this bath are the preferred salts for the present compositions, and are typically present in the range of about 30 to 225 g/l, yielding a specific gravity of at least 8° Baume. Their function appears to be one of augmenting the stability of the baths. The preferred pH for both the nickel and cobalt baths is between 3.8 and 4.3, but the acceptable range is more generally between 3 and 6. At a pH of 3.8 the efficiency of the bath of Example VI was found to be as follows:

50°C	44.8 mg/AM
40°C	47.6
37°C	49.6
35°C	49.2
30°C	48.0

Further variations of the bath set forth in Example VI are indicated below in Examples VII through IX:

Examples

	VII	VIII	IX
Gold	8 g/l	8 g/l	8 g/l
Ammonium phosphate monobasic	120 g/l	120 g/l	120 g/l
Boric acid	20 g/l	20 g/l	20 g/l
Glycerine	10 ml/l	10 ml/l	10 ml/l
Aminoguanidine bicarbonate	5 g/l	5 g/l	5 g/l
Cobalt (as the complex of Example III)	1 g/l	100 mg/l	—
Nickel (as the complex of Example IV)	—	—	200 mg
pH	4.2	4.2	4.3

The efficiency observed during plating with bath VII was 35 mg/AM at 30°C; and 34 mg/AM at 40°C. The efficiency for bath VIII was 42 mg/AM at 37°C; and the efficiency of bath IX was 38–40 mg/AM at 37°C.

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, which variations in propriety, yet reside within the true scope of the instant teaching. 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. A bright gold electroplating bath, comprising:

an aqueous solution of an alkali metal gold cyanide, said gold being present in concentrations of from about 2 g/l to saturation;

between 4 mg/l and 40 grams/l calculated as the metal, of an alloying agent selected from one or more members of the group consisting of cobalt and nickel, said agent being added to said bath as a complex with at least aminoguanidine and a chelating phosphonic acid; the concentration of said aminoguanidine being from about 2 g/l to 50 g/l, and said phosphonic acid being present in sufficient quantity to complex said alloying agent;

as additional conducting and buffering agents, one or more bath soluble phosphates;

the pH of said bath being between 3 and 6, and the concentration of said conducting and buffering agents being appropriate in the presence of the remaining bath components to adjust the bath specific gravity to a desired level of from about 6° up to 20° Baume, said level being above that which would be achieved in the absence of said agents.

2. An electroplating bath in accordance with claim **1**, wherein said pH is maintained between about 3.8 and 4.3, and the specific gravity between 10° to 16° Baume.

3. An electroplating bath in accordance with claim **2**, wherein said aminoguanidine is present in concentrations of from about 5 to 25 g/l.

4. An electroplating bath in accordance with claim **1**, wherein said phosphates include from about 30 to 225 g/l of ammonium phosphate monobasic, to yield a specific gravity of at least 8° Baume.

5. An electroplating bath in accordance with claim **4**, further including as additional stabilizers from about 1 to 50 g/l of boric acid, and from about 1 to 30 g/l of glycerine.

6. An electroplating bath in accordance with claim **1**, wherein said alloying agent comprises between 10 mg/l and 5 grams/l of cobalt, and said phosphonic acid comprises amino-trimethylenephosphonic acid.

7. An electroplating bath in accordance with claim **1**, wherein said alloying agent comprises between 10 mg/l and 5 grams/l of nickel, and said phosphonic acid comprises ethylenediamine tetra methylenephosphonic acid.

8. A method for electroplating bright deposits of gold alloyed with a metal selected from the group consisting of cobalt and nickel, comprising:

preparing a complex of a metal selected from the group consisting of cobalt and nickel, with at least aminoguanidine and a chelating phosphonic acid;

preparing an aqueous electroplating bath of an alkali metal gold cyanide, together with said complex, and as conducting and buffering agents one or more bath soluble phosphates; the pH of said bath being between 3 and 6, and said gold being present in concentrations of from about 2 g/l to saturation, said complex including in said bath from about 4 mg/l to 40 g/l of said alloying metal; the concentration of said aminoguanidine being from about 2 g/l to 50 g/l, and said phosphonic acid being present in sufficient quantity to complex said alloying metal; and the concentration of said conducting and buffering agents being appropriate in the pres-

ence of the remaining bath components to adjust the bath specific gravity to a desired level of from about 6° up to 20° Baume, said level being above that which would be achieved in the absence of said agents; and

electrolyzing said aqueous bath to yield the desired electroplating.

9. A method in accordance with claim **8,** wherein the pH of said bath is maintained between about 3.8 and 4.3, and the specific gravity between 10° and 16° Baume.

10. A method in accordance with claim **9,** wherein as further stabilizers, between about 1 to 50 g/l of boric acid, and from about 1 to 30 g/l of glycerine, are present in said bath.

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