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[54] **BATHS FOR ELECTRODEPOSITION OF GOLD AND GOLD ALLOYS AND METHOD THEREFORE**

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

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

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Polyethyleneimines, derived from the polymerization of ethylene imines, substituted ethylene imines, or derived from the addition of ethylene imine to organic or inorganic molecules, are incorporated into gold and gold alloy plating baths as agents for the general improvement of the brightness of the electroplate and other physical properties of both the deposit obtained in the electroplating from such baths and of the operating conditions of the baths. The operating characteristics of the aqueous electroplating baths such as the maximum current density, the cathode current efficiency, the width of the pH range etc. are vastly improved over conventional plating baths. Furthermore, the incorporation of these polyethylene imines also results in minimizing the stress of the electrodeposit and in minimizing the variation of the stress with current density.

15 Claims, No Drawings

BATHS FOR ELECTRODEPOSITION OF GOLD AND GOLD ALLOYS AND METHOD THEREFORE

BACKGROUND OF THE INVENTION:

The alkaline amines have been suggested for use as brightening agents in electroplating baths containing a variety of metals. Generally, these amines have included ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, and pentaethylene hexamine, and related homologous compounds based on propylene and isopropylene diamine. These compounds (Note: U.S. Pat. No. 2,817,627; U.S. Pat. No. 2,813,066; and U.S. Pat. No. 2,967,135) have limited utility and have had limited commercial acceptance because of their limited utility. Their incorporation into gold plating and gold alloy plating formulations causes an instability of the solution and a variability of the deposits from these solutions. The oxidation of the polyamines results in a gradual darkening of the solution until the solution becomes virtually opaque. Besides the inconvenience of not being able to watch the parts during plating, the oxidation products of the polyamines are occluded into the gold or gold alloy deposit and adversely affect the physical structure, corrosion and temperature resistance of the plate and adversely affect the electrical conductivity and solderability of the deposit. These adverse effects are cumulative and the increased quantities of polyamine oxidation products result in increased difficulty in maintaining consistent quality of the deposit. The darkening of the solution often results in decreased cathode current efficiency, that lengthens the time of plating a given thickness of deposit, it results in narrowing the current density range, resulting in more difficulty in maintaining the bath and limiting the speed of plating.

In view of the difficulties above described in the incorporation of polyalkyleneamines in gold and gold alloy plating baths, it was totally unexpected that the incorporation of polyethylene imines should have a beneficient effect on gold and gold alloy plating baths, and none of the maleficent effects. Further, it was unexpected that the polyethylene imines would exercise their beneficial effects in cyanide gold plating baths, whether they were operated in the acid, neutral or alkaline range, as well as on gold and gold alloy plating baths that contained non-cyanide gold salts. Although we do not wish to be limited by any theoretical considerations, it appears that the straight chain structures of the polyalkyleneamines are unsuited for the objectives of this invention and the highly branched structure of the polyethyleneimines are responsible for the beneficial effects of this invention.

Accordingly, it is an object of this invention to provide gold and gold alloy electroplating baths of improved formulations, generally operable over wider ranges of variables than conventional formulations.

Other objects and advantages will in part be obvious and in part appear hereinafter.

SUMMARY OF THE INVENTION:

This invention is concerned with electrodeposition of gold and gold alloys, using the conventional metals which are generally alloyed with gold in electrodeposits, such, for example, as copper, silver, nickel, cobalt, arsenic, indium, and others, depending upon the use intended for the plate. The invention is characterized by operation of a bath which may be virtually any standard composition for electrodepositing gold or gold alloys, which bath has incorporated therein, a polyimine compound having molecular weight in the range from about 100 – 60,000, with emphasis on the lower molecular weight range from about 100 to 2,000 as the most useful water soluble range.

Polyethyleneimine compounds can be generally classified as polymers which are cationic and highly reactive. They are formed by the polymerization of ethylene imines, substituted ethylene imines, or derived from the addition of ethylene imine to organic or inorganic molecules. The polymerization is generally achieved by acid catalysis by a variety of methods as described in Chapter 4, "Ethyleneimine and Other Aziridines" by O. C. Dermer and G. E. Ham. The chemical structure of the polyethylene imines is described in the cited references.

The discussion of the physical chemistry of these polymeric materials may be found in the technical publications of the Dow Chemical Company, Midland, Mich.

The mechanism by which the polyethyleneimines function in the plating baths is the subject of some theoretical speculation, but apparently as useful a theory as any is that the material in solution serves as a screen or sieve near the electrode and promotes or induces an orderly deposition of metal ions forming the plate, thereby producing a deposit having substantially enhanced physical properties.

The invention, therefore, is broadly directed to plating baths containing polyethyleneimines, polypropyleneimines, polyhydroxethyleneimines, polyethyleneimine adducts and ethyleneimine adducts and like polyimine compounds for the electrodeposition of gold and gold alloys and to methods of electrodeposition of gold and gold alloys wherein such baths modified in accordance with our invention are operated under conditions not operable with conventional baths.

The invention includes the addition of the polyethyleneimines to aqueous gold plating baths for the deposition of pure gold and gold alloys for jewelry, watch cases, optical, decorative and industrial electroplating. The plating baths containing the polyethyleneimines not only provide the gold and the gold alloy deposits for which they are designed, with general attendant operational advantages not obtained without the polyethyleneimines, but with the polyethyleneimines produce gold base alloy deposits and gold deposits which are brighter and have better physical properties than those obtained with the use of conventional additives.

The invention also includes the addition of polyethyleneimines together with organic and inorganic acids such as phosphoric, phosphonic, phosphinic, citric, malic, formic, and polyethyleneaminoacetic acids, and in conjunction with brightening and grain refining agents such as base metal salts, compounds or chelates such as cobalt or nickel sulfates or chelates of base metals with nitrilotriacetic acid or ethylenediaminetetracetic acid and the like. The effect of the added material is to broaden the pH range of operability of the bath, enhance the brightness of the deposit, and also to enable the bath to plate at greatly increased speeds by permitting a higher limiting current density and at a higher cathode current efficiency.

The plating baths modified with polyethyleneimines in accordance with the invention may be effectively used over a wide range of pH depending upon the de-

mand for the ultimate deposit. Generally, the bath will consist of a source of gold such as a gold cyanide or a gold sulfite, an electrolyte such as phosphates, citrates, sulfites, phosphonates, malates, tartrates or combinations of these and optional additives such as polyaminoacetic acids, organic phosphinic acids, phosphonic acids or carboxymethylated derivatives of organic phosphonic acids. Gold alloy plates may be obtained by incorporating nickel, cobalt, iron, zinc, silver, cadmium and indium or other metal ions used for this purpose.

Thus, the plating baths which are virtually any conventional aqueous cyanide or non-cyanide plating baths, which are characterized by the presence of gold in a complex form may be used over a broader range of pH, depending on the alloying metal to be plated and the particular formulation of the conventional bath for using it. Through the use of the polyethyleneimines or ethyleneimine adducts in accordance with our discovery, pH range may be extended from the strongly acid range into the strongly alkaline range, (pH 1 - 14). Generally, for most plating processes, pH's from about 3.0 to 11 are most convenient for use. Temperatures from 20° – 90°C are useful, though conventional operating temperatures is about 160°F (about 70°C).

The process in accordance with this invention is thus particularly useful for the preparation of white golds which are characterized by being basically alloys of silver and gold or nickel and gold. These are particularly desirable in the marketplace as white golds. The silver gold alloy is additionally useful as a non-tarnishing silver. Prior to our invention, baths for the deposition of so-called white golds were not commercially acceptable. We have found that with the polyethyleneimines in the proportions which we recommend, the plating baths are much improved in their production performance, speed of plating, and efficiency. The deposits from these baths exhibit reduced stress. High current efficiency and high current densities are always useful, because they allow the deposit to be made rapidly. Improved deposition with low stress gives a stable deposit which does not peel.

In the deposition of gold alloys, such as those with silver and nickel, and others, we have found that the composition of the alloy deposit is more consistent over a range of current densities. That is, there is a more consistant composition deposited from the bath over a wide range of current density and plating conditions.

With the use of certain brighteners, for example, the use of cobalt and nickel chelate brighteners in gold baths, which are formulated and in accordance with the conditions described in U.S. Patents issued to Parker and Powers, (U.S. Pat. No. 3,149,057 and U.S. Pat. No. 3,149,058), the usefulness of the bath is extended into a higher range approximating the neutral, that is, about 6 to 8. Normally, with a cobalt chelate brightener, it is not possible to go above a pH 5 without loss of brightness. However, with the use of a polyethyleneimine, the range is extended to 8 without diminution of brightness.

In conventional alkaline gold cyanide plating baths, similarly, the effectiveness of polyethyleneimines shows in the appearance of a bright and semibright range and a greatly extended lemon yellow matte plating range and virtually a tripling of the plating rate.

Accordingly, in this invention, the polyetheyleni-mines are used in any gold alloy plating bath using any brightener and performance will be enhanced in the deposition of 24 karat down to 10 karat gold plate in thicknesses up to and exceeding 40 microns (1600 millionths of an inch). In accordance with the invention, the process involves the electrodepositing of gold or gold alloy on a basis metal from an aqueous solution of at least one water soluble gold salt, in which gold solution there is dissolved from about 0.005 gram to one hundred grams per liter of the polyethyleneimine having a molecular weight in the range from about 100 to 60,000 with preferably the lower molecular weight compounds in range from about 100 to 2,000. The concentration of the material is at a useful and maximum efficiency in the order of 0.01 to 30 grams per gallon, although it is feasible and actually preferable to prepare it for some purposes in concentrations up to 100 grams per gallon.

The following outlines the group of imine compounds useful in accordance with this invention:

TYPICAL AZIRIDINE MONOMERS

Ethylene imine
Propylene imine
1-(2-hydroxyethyl)aziridine
1-(2-hydroxypropyl) aziridine
1-alkylaziridines
Aziridine-1-carboxylic esters and amides
1-arene sulfonyl aziridines
1-methyl aziridine
1-ethyl aziridine
1-n-butyl aziridine
1-phenyl aziridine
N-methyl propylene imine
N-n-butyl propylene imine
N-2 hydroxyethyl propylene imine

TYPICAL POLYETHYLENIMINES

PEI - 3*
PEI - 6*
PEI - 12*
PEI - 18*
PEI - 600*
PEI - 600E*
XD - 1363*
XD - 1035*
Poly (1-butylaziridine)
Poly (2-methylaziridine)
Poly (1-aziridine acetic) acid
Poly (S)-2-isobutylaziridine
Poly 1-alkyl aziridine
Poly (1-methylaziridine)
Poly (1-ethylaziridine)
Polypropylenimine

* Dow Chemical Co., Midland, Mich.
PEI: Trademark for polyethyleneimines.

TYPICAL ETHYLENIMINE ADDUCTS

1. Tris (2-aminoethyl) amine
2. N,N^{I}-Tetra (2-aminoethyl) ethylenediamine
3. N,N^{I},N^{II}-Penta (2-aminoethyl) diethylenetriamine
4. N,N^{I},N^{II},N^{III}-Hexa (2-aminoethyl) triethylenetetraamine
5. N,N^{I},N^{II},N^{III},N^{IIII}-Hepta (2-aminoethyl)tetraethylenepentamine

From the foregoing listing of compounds it will be apparent that a wide variety of imine compounds is useful in the improvement of the aqueous solutions for electroplating purposes. As it is pointed out the benefits ap-

pear in the formation of the bright hard gold plate under conditions which would be departures from the approved or best conditions for the use of conventional formulations. Thus, in the conventional cyanide formulation departure substantially into the acid ranges becomes possible using the polyethyleimine additives in the solution. This is illustrated in the tabulations submitted herewith. Similarly, operation in a temperature range significantly different from that which is recommended also becomes possible. Most significant is the operation at different current densities which generally bespeak a high efficiency for the solution in that higher current densities become possible.

In general all of the operations reported in the following tables used the following test technique:

Hull cell samples, at least, were conducted under the conditions specified, employing baths with the compositions shown and the reported result represents a typical result obtained under the conditions indicated. In all situations it was desired to observe the effectiveness of the imine additive in conventional solution or conventional formulation and in improved adjusted forms and this is indicated in the Tables.

The conditions and descriptions of the baths, the ingredients listed, show also the pH temperature, current density and current efficiency. Accordingly, the several baths are all individually accurately described.

Reference to the Tables for detailed conditions and results will follow:

All concentrations in the tables are in terms of the weight unit given per gallon.

For converting troy ounces per gallon to grams per liter the factor is ounces per gallon × 8.217.

For converting grams per gallon to grams per liter the factor is grams per gallon ÷ 3.785.

For converting amperes per square foot to amperes per square decimeter the factor is amperes per square foot ÷ approximately 10.

TABLE I (ALL CONCENTRATIONS ARE PER GALLON)

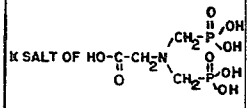
BATHS →	STANDARD GOLD	STANDARD GOLD	BATH A	BATH B	BATH B'	BATH B[a]	BATH B[b]
GOLD AS $KAu(CN)_2$	1 TR. OZ.	1 TR.OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.
KH_2PO_4	6 OZ	—	6 OZ.	6 OZ.	6 OZ.	6 OZ.	6 OZ.
$K_3C_6H_5O_7$	16 OZ.	16 OZ.	16 OZ.	16 OZ.	16 OZ.	16 OZ.	16 OZ.
K SALT OF 	—	16 OZ.	—	—	—	—	—
$H_3C_6H_5O_7$	2 OZ.	—	2 OZ.	2 OZ.	2 OZ.	2 OZ.	2 OZ.
PEI-6	—	—	10g	100g	—	—	—
PEI-12	—	—	—	—	10 g	—	—
PEI-18	—	—	—	—	—	10g	—
PEI-600	—	—	—	—	—	—	10 g
PH	6	6	6	6	6	6	6
TEMP.	160° F	160° F	160° F	160° F	160° F	160° F	160° F
C.D. (ASF)	0.5-10 LEMON YELLOW 10-20 FOXY DARK	0.5-15 SEMI BRIGHT 15-20 MATTE 20-30 FOXY BROWN	0.25-20 BRIGHT 20-35 SEMI BRIGHT 35-50 MATTE	0.25-20 BRIGHT 20-50 SEMI-BRIGHT 50-70 OK	.25-25 BRIGHT 25-100 SEMI BRIGHT	.1-25 BRIGHT 25-100 SEMI-BRIGHT	.2-100 BRIGHT
% C.E.	85 % AT 10 ASF	58% AT 15 ASF 70% AT 10 ASF	87% AT 20 ASF	96 % AT 20 ASF	54% AT 25 ASF	30% AT 50 ASF	30% AT 25 ASF

TABLE II

(ALL CONCENTRATIONS ARE PER GALLON)

Baths →	STANDARD CITRATE	BATH C
GOLD AS $KAu(CN)_2$	1 TR. OZ.	TROY OZ.
$K_3C_6H_5O_7$	16 OZ.	16 OZ.
$H_3C_6H_5O_7$	2 OZ.	2 OZ.
PEI — 6	—	10 g
pH	5-6	6
TEMP.	140-160°F.	160°F.
C.D.(ASF) 0.25-20	0.25-20 SEMI BRIGHT 20-30 MATTE 30-35 FOXY BROWN	BRIGHT 20-35 SEMI BRIGHT
% C.E.	85 % AT 15 ASF	85 % AT 15 ASF

TABLE III

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	99.8% Co–Au	BATH D	99.5 Co GOLD	BATH E	BATH EM	BATH EM'	BATH EM''
GOLD AS $KAu(CN)_2$	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.	1TR. OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.
$K H_2PO_4$	6 OZ.	6 OZ.	—	—	—	—	—
$K_3C_6H_5O_7$	10.5 OZ.	10.5 OZ.	12 OZ.	12 OZ.	—	—	—
$(NH_4)_2C_6H_6O_7$	—	—	—	—	8 OZ.	8 OZ.	8 OZ.
$H_3C_6H_5O_7$	7.5 OZ.	7.5 OZ.	8 OZ.	8 OZ.	8 OZ.	8 OZ.	8 OZ.
HCOOH	—	—	—	—	50 ml.	100 ml.	150 ml.
CoNTA	4 g	4 g	—	—	—	—	—
$CO(SO_4)_2$	—	—	¼ g.	¼ g	4 g	4g	4g
PEI—6	—	10 g	—	15 g	.01 g	1 g	10 g
pH	4.2	6	4.5	5.5	4.0	4.0	4.0
TEMP.	80°F.	100°F.	90°F.	90°F.	120°F.	120°F.	120°F.
C.D. (ASF)	0.25–20 BRIGHT 20–30 SEMI BRIGHT 30-AND UP BURN	0.25–100 BRIGHT 100–150 FOXY BROWN	0.25–20 BRIGHT 20–30 SEMI BRIGHT	0.25–100 BRIGHT 100–140 SEMI BRIGHT	0.25–50 BRIGHT 50–70 SEMI BRIGHT 70–100 MATTE	0.25–50 BRIGHT 50–70 SEMI BRIGHT 70–100 MATTE	0.25–50 BRIGHT 50–70 70–100 MATTE
% C.E.	30% AT 10 ASF 35% AT 3 ASF	40% AT 10 ASF 10% AT 100 ASF	32% AT 10 ASF 36% AT 3 ASF	38% AT 10 AS 10% AT 100 ASF	73% AT 10 ASF 13% AT 70 ASF	61% AT 10 ASF 11% AT 70 ASF	57% AT 10 ASF 10% AT 70 ASF

TABLE IV

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	STANDARD HOT CYANIDE BATH	BATH E	BATH E'	BATH E''	BATH E'''
KCN	6 OZ.	6 OZ.	6 OZ.	6 OZ.	6 OZ.
K_2HPO_4	6 OZ.	6 OZ.	6 OZ.	6 OZ.	6 OZ.
GOLD AS $KAu(CN)_2$	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.
PEI — 6	—	10 g	—	—	—
PEI — 12	—	—	10 g	—	—
PEI — 18	—	—	—	10 g	—
PEI — 600	—	—	—	—	10 g
pH	>10	>10	>10	>10	>10
TEMP.	160°	160°	160°	160°	160°
C.D. (ASF)	0.25–5 MATTE 5–10 FOXY BROWN OVER 10 BURN	O.25–10 SEMI BRIGHT TO BRIGHT 10–15 MATTE 15–20 FOXY BROWN	0.25–5 SEMI BRIGHT TO BRIGHT 5–15 MATTE 15–20 FOXY BROWN	0.25–5 SEMI BRIGHT TO BRIGHT 5–15 SEMI BRIGHT 15–20 FOXY BROWN	0.25–5 SEMI BRIGHT TO BRIGHT 5–10 MATTE 10–20 FOXY BROWN
% C.E.	90 % AT 5 ASF	90 % AT 10 ASF	81 % AT 5 ASF	80 % AT 15 ASF	65 % AT 5 ASF

TABLE V

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	BATH L	BATH L'	BATH L''
GOLD AS $KAu(CN)_2$	1 TR. OZ.	1 TR. OZ.	1 TR. OZ.
DEQUEST 2041	625 g	625 g	570 g
$K_3C_6H_5O_7$	—	—	355 g
TEPA	95 g	—	—
KOH	400 g	400 g	400 g
PEI — 6	—	95 g	—
PEI — 18	—	—	75 g
pH	7.4	7.4	6.0
TEMP.	160°F.	160°F.	140°F.
C.D.	0.25–5 SEMI BRIGHT 5–10 MATTE	0.25–25 BRIGHT 25–75 SEMI BRIGHT 75–100 MATTE	0.25–20 BRIGHT 20–75 SEMI BRIGHT 75–100 MATTE
% C.E.	90 % AT 5 ASF	80 % AT 25 ASF	80 % AT 20 ASF

TABLE VI

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	STANDARD BATH	BATH F	BATH F'	BATH FM
GOLD AS $KAu(CN)_2$	1.5 TR. OZ.	1.5 TR. OZ.	1.5 TR. OZ.	1.0 TR. OZ.
SILVER AS $KAg(CN)_2$	6.5 g	6.5 g	6.5–10 g	15 g
COBALT AS $KCo(CN)_3$	2.5 g	2.5 g	2.5 g	—
K_2HPO_4	12 OZ.	12 OZ.	12 OZ.	—
DEQUEST 2041	—	—	—	10 OZ.
8-DIHYDROXYNAPTHALENE 3,6-DISULFONIC ACID	—	—	2 g	—
PEI — 6		4 g	25 g	10 g
pH	10	10.2	10.2	8.5
TEMP.	70°F.	70°F.	70°F.	100°F.
C.D.(ASF)	6–10 SEMI-BRIGHT	1–15 BRIGHT	1–15 BRIGHT	3–20 BRIGHT
C.D. (ASF)	3–5 DULL (MEDIUM STRESS)			

TABLE VII

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	STANDARD BATH	BATH G
GOLD AS $KAu(CN)_2$	10 g	10 g
GLYCINE	17 OZ.	17 OZ.
$K_3C_6H_5O_7$	4 OZ.	4 OZ.
$NiSO_4$	5½ OZ.	5½ OZ.
PEI — 6	—	5 g
pH	4	4.5
TEMP.	120°F.	120°F.
C.D.(ASF)	3–20 DARK BRIGHT	3–30 WHITE BRIGHT
C.D. (ASF)	20–30 DARK 10% AT 10 ASF	30–40 GRAY 10% AT 10 ASF
% C.E.	7% AT 20 ASF	7% AT 20 ASF

TABLE VIII

(ALL CONCENTRATIONS ARE PER GALLON)

BATHS →	BATH H	BATH H'	STANDARD BATH
GOLD AS $Na_3Au(SO_3)_2$	1.5 TR. OZ.	1.5 TR. OZ.	1.5 TR. OZ.
Na_2SO_3	6 OZ.	6 OZ.	6 OZ.
AS	120 ppm	—	—
PEI — 6	—	10 g	—
pH	9½	9½	9½
TEMP.	130°F.	130°F.	130°F.
C.D. ASF	1–8 BRIGHT	1–8 BRIGHT	1–8 MATTE
%	1–8 ASF IS 95–100%	1–8 ASF IS 80–90%	1–8 ASF IS 80–90%

Referring now to the Tables, it will be apparent that the additives give certain beneficial results to the plating operations.

Thus, in Table I there is employed a standard aqueous gold cyanide solution. In fact, the material is shown to be standard gold or a slightly improved standard gold. It will be apparent that in the first two columns of the Table the formulations for the baths are substantially the same, the improved standard gold containing a nitrilophosphinic acid and potassium salt of monoaceticphosphinic nitrilo acid. Details of such baths are given in Florence P. Butler and Alfred M. Weisberg, Application Ser. No. 327,690 filed Jan. 29, 1973, Preparation of Aminopolymethylene Phosphinic; Alfred M. Weisberg and Florence P. Butler, Application Ser. No. 327,681 filed Jan. 29, 1973, Process for Producing Bright Electrodeposits of Gold and Its Alloys; Alfred M. Weisberg and Harry Kroll, application Ser. No. 319,157 filed Dec. 29, 1972, Process for Producing by Electrodeposition Bright Deposits of Gold and Its Alloys, as a continuation of Alfred M. Weisberg and Harry Kroll, Application Ser. No. 166,030 filed July 26, 1971, Process for Producing by Electrodeposition Bright Deposits of Gold and Its Alloys, now abandoned.

It will be apparent from Bath A and B which are characterized by the presence of 10 grams and 100 grams of polyethyleneimine, respectively, that operation gave good bright conditions at higher current density than under the ordinary conventional formulation. The current efficiency also indicated a substantial improvement.

The column labeled Bath B' is a modification of Bath B using a different polyethyleimine and showing results in substantially the same improved range.

Bath B^a and B^b, modified as per A, show a somewhat different polyethyleneimine gives good bright plating at a high current density with moderate current efficiency.

In Table II there is a comparison of a standard citrate bath with a modified citrate bath employing polyethyleneimine, showing that significantly improved plating conditions and results are obtained.

In Table III there is summarized a comparison of a gold plating bath using a cobalt nitrilotriacetic acid

chelate brightener with a modified bath employing the same brightener and 10 grams of polyethyleneimine. It is quite apparent in the report of current density and pH that operation under significantly different conditions becomes possible with equally good results.

In Table IV extended hot cyanide bath for plating gold is compared with the same bath modified with polyethyleneimines operating in all cases at 160°F, but it will be observed that, in general, the current density which became possible was substantially extended. That is, the operation under the indicated additive agent and at the temperature shown at the pH indicated gave a substantially higher current density possibility for the bath.

Table V, upon analysis of the comparison of a gold bath with conventional gold, with a phosphonic acid complexing agent, and then modified with a polyethyleneimine, again shows an extension of the range of current density by a factor of about 5.

Table VI similarly compares the standard cyanide gold with silver. This is a silver gold alloy plating solution with a modified form of the same, wherein polyethyleneimine is employed in the modified gold plating bath with the result that significantly improved results are observed.

In Table VII gold cyanide in a conventional nickel formulation in a nickel gold formula, a variant of the white gold, is compared with polyethyleneimine additive with the standard formulation to point out that a significantly increased range of brightness is achieved.

Table VIII which compares a gold cyanide and sulfite bath with the same bath modified with polyethyleneimine demonstrates that the operation at about the same current density is possible but there is developed a bright coating and this is done at a current efficiency of 90 percent.

It will be apparent from the inspection of the results which can be repeated many times over that the basic improvement which Applicants achieve in the operation of the plating baths is that the pH range of operation will be expanded, the temperature range will be widened, and that the application of the gold to industrial and to ornamental purposes through the ornamentation of surfaces is improved in that generally greater latitude in operation becomes achievable.

What is claimed is:

1. An aqueous bath for electrodeposition of gold and gold alloys comprising, in said bath,

gold in solution as a water soluble compound thereof,

alloying metal as a salt in an amount from 0 to 20 grams of metal per liter of solution,

electrical conductivity enhancing electrolyte selected from the group consisting of phosphoric, phosphonic, phosphinic, citric, malic, formic, and ethylene polyamino acetic acids in amount from about 6 to 16 ounces per gallon of solution,

a compound selected from the group consisting of polyethyleneimines derived from polymerized ethyleneimine, substituted ethyleneimines or polyethyleneimines derived from the addition of ethyleneimine to organic or inorganic molecules,

said imine compound being present in amount from 0.005 to 100 grams per liter of bath and said compound having a molecular weight in the range from 100 to 60,000,

said bath being adjusted to pH operating level in the range from 1 to 14.

2. A bath in accordance with claim **1** wherein the gold is present in solution as the potassium gold cyanide.

3. A bath in accordance with claim **2** wherein the imine compound has a molecular weight of about 600 present in solution with the potassium gold cyanide.

4. A bath in accordance with claim **1** wherein the gold is present in solution as a complex gold sulfite.

5. A bath in accordance with claim **4** wherein the imine compound has a molecular weight of about 600 present in solution with a complex gold sulfite.

6. A bath in accordance with claim **1** wherein the gold is present in the solution as a sodium gold cyanide.

7. A bath in accordance with claim **6** wherein the imine compound has a molecular weight of about 600.

8. A bath in accordance with claim **1** wherein the gold is present in the solution as a complex ammonium gold cyanide.

9. A bath in accordance with claim **1** wherein the solution contains a phosphinic acid agent.

10. A bath in accordance with claim **1** wherein the solution contains a phosphinic-carboxylic acid agent.

11. A bath in accordance with claim **1** wherein the solution contains a phosphonic-carboxylic acid agent.

12. A bath in accordance with claim **2** in which the bath contains a cobalt and/or nickel chelate compound.

13. A bath in accordance with claim **1** in which the bath contains a polyamine.

14. The method of electroplating gold or gold alloy to form a bright hard deposit which comprises

in an aqueous bath for the electrodeposition of gold having gold present therein as cyanide or sulfite in solution in a concentration in the range from 0.05 grams per liter of gold to saturation and an alloying metal as a salt in an amount from 0 to 20 grams of metal per liter of solution

incorporating in said solution an imine compound selected from the group consisting of

polyethylene imines derived from polymerization of ethylene imine;

ethylene imine and substituted ethylene imine and imines derived from addition of ethylene imine to organic or inorganic molecules, said imine compound being incorporated in amount from 0.005 to 100 grams per liter and having a molecular weight in the range 100 to 60,000

and electroplating gold or gold base alloy from said solution onto a base metal while maintaining the pH of the solution in the range from about 1 to 14 and employing a current density of ½ to 100 amperes per square foot at a temperature in the range from 20°C to 90°C.

15. The method in accordance with claim **14** in which the alloy metal is silver and a silver-gold alloy is deposited on flatware and hollowware.

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