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Greenspan

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[54] **GOLD PLATING SOLUTIONS AND METHOD**

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[51] **Int. Cl.²** **C25D 3/62**

[58] **Field of Search** ..... 204/43 G, 44, 46 G; 106/1; 117/130 E

[56] **References Cited**

UNITED STATES PATENTS

2,724,687	11/1955	Spreter et al.	204/43 G
3,149,057	9/1964	Parker et al.	204/46 G
3,149,058	9/1964	Parker et al.	204/46 G
3,174,918	3/1965	Rinker et al.	204/43 G
3,666,640	5/1972	Smith	204/44
3,783,111	1/1974	Bick et al.	204/46 G

Primary Examiner—G. L. Kaplan

[57] **ABSTRACT**

An aqueous gold plating solution for use in depositing bright gold plating is provided, which includes an alkali gold cyanide as the gold source, a metal chelate of an iminodiacetic acid, such as the indium or nickel chelate of iminodiacetic acid, which metal codeposits in small quantities with the gold, one or more conducting salts and a buffer, to maintain said solution at a pH within the range of from about 3 to about 4.5. The aqueous gold plating solution may optionally include a metal chelate of an aminopolycarboxylic acid, such as the nickel chelate of ethylenediamine tetraacetic acid. In addition, a method of electrodepositing gold on a substrate employing the gold plating solutions described above and gold-plated substrates or articles produced thereby are also provided.

A synergistic chelate combination employed in the aforedescribed gold plating solutions to produce mirror bright gold finishes is also provided, which combination includes the nickel chelate of iminodiacetic acid, the nickel chelate of ethylenediamine tetraacetic acid and the cobalt chelate of iminodiacetic acid.

30 Claims, No Drawings

GOLD PLATING SOLUTIONS AND METHOD

The present invention relates to gold plating solutions. In its more specific aspect, this invention relates to gold plating solutions and to the method of gold plating using these solutions to obtain bright gold finishes and to gold-plated articles produced thereby.

Gold plating by electrodeposition employing a gold plating bath or electrolyte is a long known and widely used technique. However, in recent years, the price per ounce of gold has soared making the cost of gold practically prohibitive and resulting in a concomitant increase in the price of gold-plated articles. Nevertheless, the demand for such gold-plated articles is increasing. This is particularly true of gold-plated articles which for all practical and aesthetic purposes take on the appearance of pure gold articles, that is, articles which have a hard, pale-colored, smooth, mirror-bright surface.

Over the years, gold plating has been carried out primarily employing an electrolytic bath containing an alkali metal aurocyanide as the gold source, which may also include other soluble metal salts. One such type of electrolytic bath is operated on the alkaline side, and is usually maintained at a pH in the range of 8 to 12 so as to avoid formation of the extremely toxic hydrogen cyanide gas as well as the possible formation of insoluble aurous cyanide.

An efficient electroplating operation utilizing the alkaline electrolytic baths described above, must operate at relatively high temperatures and usually at rather low current densities. Under these conditions, it is difficult to obtain thick bright gold deposits, that is, a deposit having a thickness greater than 50 microinches. It, therefore, has been common practice to add to such an alkaline bath certain soluble metal salts which are codeposited with the gold to impart certain desirable qualities to the plate such as color, hardness and wear resistance.

It is also known to employ gold plating baths on the weak acid side, for example, at a pH ranging from 3 to 5, wherein alkali metal aurocyanide is employed as the source of gold. Such a technique and bath are disclosed in U.S. Pat. No. 2,905,601 to Rinker et al. The problem of hydrogen cyanide gas formation is overcome by employing with such baths a weak stable organic acid, such as acetic acid, citric acid, tartaric acid, lactic acid or similar acids which may be neutralized with ammonium hydroxide to give the desired pH. These baths also include one or more soluble base metal salts, a portion of the metal of which codeposits with the gold to produce a plate of the desired color and thickness.

Unfortunately, it has been found that where weak organic acids are employed in gold plating baths such as disclosed in U.S. Pat. No. 2,905,601, oxidation at the insoluble anode occurs producing organic decomposition products which discolor the bath and adversely affect the resulting plate.

British Pat. No. 919,463 which relates to the electroplating of bright gold, discloses an improvement over the technique and bath disclosed in U.S. Pat. No. 2,905,601. The improvement resides in the inclusion of a metal compound in the form of a soluble metal compound or chelate (in place of the base metal salts of U.S. Pat. No. 2,905,601) which ionizes to produce metal ions in the electrolytic bath in sufficient quantity to codeposit with the gold to give bright metal alloy deposits. The only examples of the soluble metal compound or chelate disclosed are nickel dimethylethanolamine and cobalt triglycollamate.

U.S. Pat. No. 3,149,057 to Parker et al discloses acid gold plating baths which include an alkali metal aurocyanide as the gold source, with or without additional alloying salts, the cobalt chelate of ethylenediamine tetraacetic acid, or a cobalt chelate of a chelating agent having a stability constant of about the same order of magnitude, and at least one buffer material to maintain the pH between 3 and 4.5 during the deposition of the gold from the solution. This patent indicates that the cobalt chelate is such that cobalt is not deposited under plating conditions, but that the cobalt chelate is employed to form a complex with the alkali metal gold cyanide so that hydrogen cyanide will not be released even when the pH of the bath is maintained between 3 and 5. The bath may also include metal salts chelates or complexes, wherein the metal component thereof will plate out; examples of such compounds disclosed are antimony tartrate, nickel or cadmium ethylenediamine tetraacetic acid and similar compounds of indium, zinc, copper and iron.

U.S. Pat. No. 3,149,058 to Parker et al discloses a gold plating bath which includes an alkali metal aurocyanide, with or without additional alloying components, the nickel chelate of an appropriate polycarboxylic acid, having a stability constant of the order of magnitude of about 10, and at least one buffer material to maintain the pH between 3.5 and 5.5 during the deposition of the gold from the solution. As indicated in working Example II thereof, only about 0.18 percent nickel is present in the gold plate.

It has been found that where alkali metal gold cyanide is employed in a gold plating bath with nickel or cobalt chelates of aminopolycarboxylic acids, with or without other alloying components, as disclosed in the aforedescribed British Pat. No. 919,483 and U.S. Pat. Nos. 3,149,057 and 3,149,058, the gold alloy deposit is not sufficiently thick to exhibit the desired brightness and color of the resulting plate, especially for decorative purposes such as in jewelry. It is theorized that the nickel, cobalt or other base metals are complexed to too high a degree to enable sufficient metal ion concentration to be available for plating purposes to produce the desired thickness and color.

In accordance with the present invention, an aqueous gold plating bath or electrolytic solution having a pH ranging from about 3 to about 4.5 is provided which is not subject to the oxidation and complexing problems associated with prior art acid gold plating baths, and produces bright gold alloy deposits of thicknesses of 200 microinches or more, possessing excellent metallurigical properties such as ductility, hardness and wear properties. The gold plating solution of the invention is a stable solution which is easily maintained, and which will provide a constant color and uniform deposition even when the temperature, pH, current density, agitation, metallic contact or anode to cathode vary. The gold alloy deposits produced in accordance with the invention require no buffing or other mechanical operations to further enhance their brightness and have a pleasing range of colors that are acceptable to the jewelry trade and are of a sufficiently high Karat to be nontarnishing.

Thus, in accordance with the present invention, there is provided an aqueous electrolytic bath for use in elec-

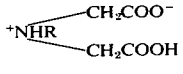
troplating gold alloys, which bath has a pH within the range of from about 3 to about 4.5 and comprises a gold cyanide as the gold source, at least one metal chelate of an iminodiacetic acid, at least a portion of the metal which ionizes and codeposits with the gold, at least one conducting salt, and a buffer to maintain said bath at the desired pH. In a preferred embodiment of the invention, the bath also includes one or more metal chelates of aminopolycarboxylic acids.

The gold cyanide, employed in the aqueous electrolytic bath as the gold source, is desirably an alkali metal gold cyanide or ammonium double cyanide of gold. Examples of such compounds include potassium aurocyanide, sodium aurocyanide and ammonium aurocyanide, and the preferred gold cyanide is potassium aurocyanide. The gold in the form of the cyanide complex present in the bath ranges from about 1 to 24 grams/liter, and preferably from about 3 to about 8 grams/liter, depending upon the thickness of gold deposit desired. Where gold concentration of less than 1 gram/liter are employed, low current densities are employed and concomitant long plating times are required to form a plate of desired thickness. Thus, the use of such low concentrations would not be commercially feasible. Although gold concentrations of more than 24 grams/liter may be employed, the resulting plate is usually too yellow in color for decorative purposes such as in jewelry.

The metal chelate of an iminodiacetic acid employed in the aqueous electrolytic bath should have a stability constant of the order of magnitude of up to about 10 so that it will ionize to produce sufficient metal ions which codeposit with the gold. The bath contains about 0.05 to about 10 grams/liter metal in the form of metal chelate of an iminodiacetic acid, and preferably from about 0.5 to about 3 grams/liter. The concentration and stability constant of these metal chelates determine the amount of metal codeposited with the gold and enhances the gold plate. If less than 0.05 grams/liter of such metal in the form of the chelate of an iminodiacetic acid is employed, the plating solution will not contain a sufficient ion concentration of such metal for codeposition with the gold to produce the desired alloy deposit. Where more than 10 grams/liter of such metal in the form of the above chelate is employed, the concentration of such metal codepositing with gold will be unduly high and may produce a plate of undesirable color. Furthermore, the specific gravity of the plating solution may be so high to cause crystallization of some of the metal chelates present therein.

Suitable metal chelates include those in which the metal portion is selected from the group consisting of indium, nickel, cobalt, zinc or cadmium.

The iminodiacetic acid portion of the metal chelate has the formula



wherein R is hydrogen or an organic radical selected from the group consisting of lower alkyl, acetamide, cyano-lower alkyl, (trilower alkylammonium) lower alkyl, N-lower alkoxy-lower alkyl, hydroxy-lower alkyl, N-carbethoxy-p-aminoethyl, N-mercapto-lower alkyl and N-lower alkylthio-lower alkyl. The term "lower alkyl" as employed in the radicals refers to straight chain or branched chain radicals of up to and including eight carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, s-butyl, t-butyl, pentyl, hexyl, heptyl, octyl and the like. The term "lower alkoxy" includes straight and branched chain radicals of the structure R^1O wherein R^1 includes any of the above lower alkyl groups.

Examples of metal chelates which may be employed in the aqueous electrolytes of the invention include the cobalt, indium, nickel, zinc or cadmium chelates of iminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-methyliminodiacetic acid, the cobalt, indium, N-methythioethyliminodiacetic zinc or cadmium chelates of N-acetamidoiminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of β-(N-trimethylammonium)-ethyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-cyanomethyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-methoxyethyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-hydroxyethyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-3-hydroxypropyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of N-carbethoxy-β-aminoethyliminodiacetic acid, the cobalt, indium, nickel, zinc or cadmium chelates of β-mercaptoethyliminodiacetic acid, and the cobalt, indium, nickel, zinc or cadmium chelates of N-methioethyliminodiacetic acid. The preferred chelates are the indium or nickel chelates of iminodiacetic acid, such as potassium nickel iminodiacetate and potassium indium iminodiacetate.

As indicated, the electrolytic bath may optionally include one or more metal chelates of aminopolycarboxylic acids which should have a stability constant ranging from about 6 to about 25. Where the metal chelate has a stability constant of less than about 6, the free ion concentration of such metal will be excessively high resulting in an uneven plate. A metal chelate having a stability constant greater than 25 will not provide a sufficient ion concentration available for codeposition. These chelates are employed to impart desired tint to the gold alloy plate. For example, where the metal chelate is an indium chelate, a portion of the indium will codeposit with the gold to provide a greenish-yellow tint to the plate. Where the metal chelate is a nickel chelate, a portion of the nickel will codeposit with the gold to provide a light or pale yellow tint to the plate. Where the metal chelate is cobalt chelate, a portion of the cobalt will codeposit with the gold to provide an orange tint to the plate. Furthermore, use of the cobalt chelate allows for use of increased current density without causing dulling of the plate. The concentration of metal chelates of the aminocarboxylic acids in the electrolytic bath ranges from 0 to about 15 grams/liter, preferably from about 0.25 to about 10 grams/liter, depending upon the tint desired in the electroplate or coating. Higher concentrations of such metal chelates do not appear to provide any additional beneficial effect. Examples of the metal chelates of aminopolycarboxylic acids suitable for use herein include, but are not limited to, nickel cobalt, indium, zinc, and cadmium chelates of ethylenediamine tetraacetic acid, hydroxyethyl ethylenediamine triacetic acid, hydroxypropyl ethlenediamine triacetic acid, ethylenediamine diacetic acid and the like. The preferred chelates are the nickel indium and cobalt chelates of ethylenediamine tetraacetic acid.

The conducting salt added to the aqueous electrolytic bath may include ammonium or alkali metal sulfamates, as well as any of the sulfates, sulfamates, formates, acetates, citrates, lactates, tartrates, fluoborates, borates, phosphates, carbonates and bicarbonates of metals such as nickel, zinc, cobalt, indium, iron, manganese, antimony, copper, alkali metals such as potassium or sodium and the like. The bath may include one, two or more of such conducting salts as long as the added salts are soluble and compatible with all other bath ingredients and will not cause undesired precipitation. For example, where an indium chelate is employed in the bath, such as the indium chelate of iminodiacetic acid, phosphate or other phosphorus containing salts should be avoided. Normally, such conducting salts will be employed in an amount within the range of from about 10 to about 150 grams/liter and preferably within the range of from about 15 to about 40 grams/liter. The concentration of conducting salts should be maintained within the above-mentioned broad range inasmuch as if the concentration thereof is below 10 grams/liter the plating solution will not be sufficiently conductive, while if the concentration thereof is above 150 grams/liter the specific gravity of the plating solution will be undesirably high with the result that one or more of the metal chelates may crystallize out of the solution.

A suitable buffer is added to the aqueous electrolyte to maintain the bath within the desired pH range of from about 3 to about 4.5. Preferably, the buffer comprises one or more organic acids which has at least one ionization constant of such a value as to create a buffer region in the above pH range. Examples of such organic acids suitable for use herein include, but are not limited to, aminoacetic acid, sulfamic acid, citric acid, citraconic acid, itaconic acid, lactic acid, gluconic acid, glutaric acid, glycollic acid, tartaric acid, acetic acid, kojic acid, formic acid and the like. In addition, inorganic acids such as boric acid, sulfuric acid, phosphoric acid and the like may be employed. The above acids may be employed in the form of salts as well.

In order to bring the electrolytic bath to the proper pH, the bath may be neutralized with an appropriate amount of base. Examples of such bases suitable for use herein include ammonium hydroxide, ammonia, alkali metal hydroxides such as potassium or sodium hydroxide and the like.

The buffer will ordinarily be employed in an amount within the range of from about 5 to about 200 grams/liter to maintain the electrolytic bath at the desired pH of from about 3 to about 4.5

and preferably from about 3.5 to about 4.2. If the plating solution is maintained at a pH below 3, some of the gold cyanide may precipitate. Furthermore, if the plating solution is maintained outside of the above pH range it will be difficult to obtain the codeposition of metals and the desired color in the plate. It will be appreciated that a smaller amount of the buffer may be required than expected where other components of the electrolytic bath also provide buffering action, such as the nickel chelate of ethylenediamine tetraacetic acid.

A plating exhibiting a mirror bright finish is achieved by adding to the electrolytic bath of the invention the nickel chelate of iminodiacetic acid, the nickel chelate of ethylenediamine tetraacetic acid and the cobalt of iminodiacetic acid. This combination of nickel chelates and cobalt chelate has a synergistic effect and produces a coating superior to one produced when the nickel chelates and the cobalt chelate are used alone, as well as the additive effect thereof. A bath using this combination of chelates produces an intense brightness and the mirror bright finish.

The nickel in the form of the nickel chelate of ethylenediamine tetraacetic acid is employed in a weight ratio to the nickel in the form of nickel chelates of iminodiacetic acid of within the range of from about 10:1 to about 0.2:1, preferably from about 5:1 to about 0.5:1. Cobalt in the form of the cobalt chelate is employed in a weight ratio to the nickel in the form of the nickel chelate of iminodiacetic acid of within the range of from about 10:1 to about 0.05:1, preferably from about 5:1 to about 0.2:1. The ratios of chelates should be maintained within the above ranges in order to obtain the desired synergism.

The electroplating process is carried out at a current density within the range of from about 1 to about 40 amperes per square foot, preferably 5 to 20, while maintaining the bath at a temperature within the range of from about 20° to about 80°C. and preferably from about 25° to about 40°C. If the current density is maintained below 1 ampere per square foot, an inordinate amount of plating time will be required in order to obtain a plate of desired thickness. On the other hand, if the current density is maintained above 40 amperes per square foot, the resulting plate will be undesirably dull and may be burnt. Furthermore, where the temperature of the plating solution is maintained at below about 20°C, the resulting plate will not have the desired brightness. Where the temperature is maintained above 80°C, the decomposition of one or more of the components of the plating solution may result.

The electrodes used may include such materials as platinum, gold, stainless steel, platinized titanium or carbon as the anode and such materials as steel, copper, nickel, brass and the like as the cathode (the wares plated). The ratio of cathode to anode surface area, while not critical, should be within the range of from about 1:1 to about 1:4 and preferably about 1:2. It is customary to agitate the bath, such as with a stirrer, or to move the work (pieces to be plated) as with a cathode oscillating rod to facilitate uniform and smooth deposition. The voltage between the anode and the wares to be plated as the cathode will usually be between 2 and 6 volts.

My invention provides a heavy plate onto a base metal or ware such as stainless steel, brass, copper, which is bright, stain resistant and corrosion resistant. The plate or coating will have a thickenss of from about 5 to about 200 microinches or more and may have a thickness of 500 microinches or more. Furthermore, where the aforedescribed synergistic combination of chelates is employed, the resulting plate will be mirror bright and will be substantially brighter than deposits produced employing baths containing one or two of the individual components of such synergistic combination. The gold alloy plate will comprise from about 90 to about 99.8% gold and from about 10 to about 0.2% of the alloying components such as indium, nickel, cobalt, zinc or cadmium or mixtures thereof. Such plate will have a Knoop hardness of at least 120 Knoop and in some cases as high as 250 Knoop.

The following working examples represent preferred embodiments of the present invention:

EXAMPLE 1

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of nickel as potassium nickel iminodiacetate
20 grams ammonium phosphate
20 grams ammonium sulfamate
10 grams aminoacetic acid

The pH was adjusted to 3.5–3.8 with phosphoric acid. A polished brass test panel 1 inch × 3 inch was plated using a current density of 5 amperes per square foot at a temperature of 35°C., for 50 minutes. A mirror bright pale yellow deposit 2.5 microns (100 microinches) was obtained, having a Knoop hardness of approximately 250. Above this thickness, a slight haziness tends to develop. Also where the current density was increased to 10 amperes per square foot the deposit tended to become dull around the edges of the panel.

EXAMPLE 2

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of nickel as potassium nickel iminodiacetate
3 grams of nickel as potassium nickel ethylenediaminetetraacetate
20 grams ammonium phosphate
20 grams ammonium sulfamate
10 grams aminoacetic acid

The pH was adjusted to 3.5–3.8 with phosphoric acid. A polished brass test panel 1 inch × 3 inches was plated using a current density of 10 amperes per square foot at a temperature of 35°C., for 25 minutes. A mirror bright pale yellow deposit 2.5 microns (100 microinches) was obtained (Knoop hardness about 250). Above this thickenss the deposit tended to become slightly hazy. Where the current density was increased to 15 amperes per square foot, the deposit tended to become dull around the edges of the panel.

EXAMPLE 3

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of nickel as potassium nickel iminodiacetate
3 grams of nickel as potassium nickel ethylenediamine tetracetate
0.1 gram cobalt as potassium cobalt iminodiacetate
20 grams ammonium phosphate
20 grams ammonium sulfamate
10 grams aminoacetic acid

The pH was adjusted to 3.5–3.8 with phosphoric acid. A polished brass panel 1 inch × 3 inches was plated using a current density of 10 amperes per square foot at a temperature of 35°C for 50 minutes. A mirror bright pale yellow deposit 5 microns (200 microinches) was obtained. Above this thickenss the deposit remained mirror bright. Another panel was plated using a current density of 15 amperes per square foot for 33 minutes yielding a plate of the same thickness and color and was mirror bright.

EXAMPLE 4

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of nickel as potassium nickel iminodiacetate
3 grams of nickel as potassium nickel ethylenediamine tetraacetate
1 gram of indium as sodium indium ethylenediamine tetraacetate
0.1 gram cobalt as potassium cobalt ethylenediamine tetraacetate
40 grams ammonium sulfamate
10 grams ammonium citrate
10 grams aminoacetic acid

The pH was adjusted to 3.5–3.8 with phosphoric acid. A polished brass panel 1 inch × 3 inches was plated using a current density of 15 amperes per square foot at a temperature of 35° for 33 minutes. A mirror bright deposit 5 microns (200 microinches was obtained). The color of the deposit was pale orange yellow. This color is a standard color, widely acceptable commercially in the jewelry trade.

EXAMPLE 5

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of indium as potassium indium iminodiacetate
10 grams of ammonium citrate
10 grams glycine (aminoacetic acid)
40 grams ammonium sulfamate

The pH was adjusted to 3.5–3.8 with sulfamic acid. A polished brass panel 1 inch × 3 inches was plated using a current density of 5 amperes per square foot at a temperature of 35°C for 15 minutes. A mirror bright greenish yellow deposit 2½ microns. (100 microinches) was obtained.

EXAMPLE 6

In an amount of water to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of zinc as potassium zinc iminodiacetate
20 grams ammonium phosphate
40 grams ammonium sulfamate
20 grams aminoacetic acid

The pH was adjusted to 4.0–4.2 with phosphoric acid. A polished brass panel 1 inch × 3 inches was plated using a current density of 5 amperes per square foot for 15 minutes. A mirror bright yellowish white deposit 2½ microns (100 microinches) was obtained.

EXAMPLE 7

In an amount to form 1 liter of solution was dissolved:

4 grams of gold in the form of potassium gold cyanide
1 gram of zinc as potassium zinc iminodiacetate
1 gram of nickel as potassium nickel iminodiacetate
20 grams ammonium phosphate
40 grams ammonium sulfamate
20 grams aminoacetic acid

The pH was adjusted to 3.8–4.2 with phosphoric acid. A polished brass panel 1 inch × 3 inches was plated using a current density of 10 amperes per square foot. A mirror bright white gold deposit of 5 microns (200 microinches) was obtained. I claim:

1. An aqueous electrolytic bath for gold plating comprising a gold cyanide as a gold source in an amount to provide a gold concentration within the range of from about 1 to about 24 grams/liter, a metal chelate of an iminodiacetic acid in an amount to provide a concentration of said metal within the range of from about

0.05 to about 10 grams/liter, at least one additional conducting salt in an amount within the range of from about 10 to about 150 grams/liter, and a buffer to maintain said electrolytic bath at a pH within the range of from about 3 to about 4.5.

2. The electrolytic bath in accordance with claim **1** wherein said metal iminodiacetic acid chelate has a stability constant of up to about 10.

3. The electrolytic bath in accordance with claim **2** wherein said metal of said metal iminodiacetic acid chelate is indium.

4. The electrolytic bath in accordance with claim **2** wherein said metal of said metal iminodiacetic acid chelate is nickel.

5. The electrolytic bath in accordance with claim **2** wherein said metal of said metal iminodiacetic acid chelate is cobalt.

6. The electrolytic bath in accordance with claim **2** wherein said metal of said metal iminodiacetic acid chelate is cadmium.

7. The electrolytic bath in accordance with claim **2** wherein said metal of said metal iminodiacetic acid chelate is zinc.

8. The electrolytic bath in accordance with claim **1,** including, in addition, a metal chelate of an aminopolycarboxylic acid in an amount to provide a concentration of said metal in an amount within the range of from about 0.25 to about 15 grams/liter.

9. The electrolytic bath in accordance with claim **8** wherein said metal chelate of an aminopolycarboxylic acid is a metal chelate of ethylenediamine tetraacetic acid.

10. The electrolytic bath in accordance with claim **9** wherein said metal chelate of ethylenediamine tetraacetic acid is the nickel chelate of ethylenediamine tetraacetic acid and the metal chelate of an iminodiacetic acid is the nickel chelate of iminodiacetic acid.

11. The electrolytic bath in accordance with claim **10,** including, in addition, the cobalt chelate of iminodiacetic acid.

12. The electrolytic bath in accordance with claim **10,** including, in addition, the indium chelate of ethylenediamine tetraacetic acid.

13. The electrolytic bath in accordance with claim **1** wherein said gold cyanide is an alkali gold cyanide selected from the group consisting of alkali metal gold cyanides and ammonium gold cyanide.

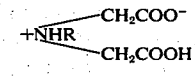
14. The electrolytic bath in accordance with claim **13** wherein said metal chelate of iminodiacetic acid is the nickel chelate of iminodiacetic acid, said bath further comprising the nickel chelate of ethylenediamine tetraacetic acid in an amount to provide a nickel concentration of within the range of from about 0.25 to about 10 grams/liter, and a chelate selected from the group consisting of the indium chelate of ethylenediamine tetraacetic acid in an amount to provide an indium concentration within the range of from about 0.25 to about 15 grams/liter, and the cobalt chelate of iminodiacetic acid in an amount to provide a cobalt concentration within the range of from about 0.05 to about 10 grams/liter, and mixtures thereof.

15. The electrolytic bath in accordance with claim **14** wherein said conducting salt comprises a water-soluble ammonium salt or alkali metal salt.

16. The electrolytic bath in accordance with claim **14** wherein said buffer comprises a weak organic acid.

17. The electrolytic bath in accordance with claim **13** wherein said alkali gold cyanide is potassium aurocyanide.

18. The electrolytic bath in accordance with claim **1** wherein said metal chelate is prepared from an iminodiacetic acid having the formula



wherein R is hydrogen or an organic radical selected from the group consisting of lower alkyl, acetamide, cyano-lower alkyl, (trilower alkylammonium) lower alkyl, N-lower alkoxy-lower alkyl, hydroxy-lower alkyl, N-carbethoxy-p-aminoethyl, N-mercapto-lower alkyl and N-lower alkylthio-lower alkyl.

19. The electrolytic bath in accordance with claim **18** wherein R is hydrogen.

20. The electrolytic bath in accordance with claim **18** wherein R is methyl.

21. The electrolytic bath in accordance wtih claim **1** wherein said buffer is present in an amount within the range of from about 5 to about 200 grams/liter.

22. A method of electroplating gold, which comprises electrolyzing an aqueous solution having a pH within the range of from about 3 to about 4.5 comprising the aqueous electrolytic bath as defined in claim **1,** to form an electroplated coating of gold and said metal of said metal chelate of an iminodiacetic acid.

23. The method in accordance with claim **22** wherein said aqueous electrolytic bath further includes a metal chelate of an aminopolycarboxylic acid in an amount to provide a concentration of said metal within the range of from about 0.25 to about 15 grams/liter.

24. The method in accordance with claim **23** wherein said metal chelate of an aminopolycarboxylic acid comprises the nickel chelate of ethylenediamine tetraacetic acid.

25. The method in accordance with claim **24** wherein said electrolytic bath further includes a chelate selected from the group consisting of the cobalt chelate of iminodiacetic acid in an amount to provide a cobalt concentration within the range of from about 0.05 to about 10 grams/liter, and the indium chelate of ethylenediamine tetraacetic acid in an amount to provide an indium concentration within the range of from about 0.25 to about 15 grams/liter, and mixtures thereof.

26. The method in accordance with claim **22** wherein said metal chelate of an iminodiacetic acid is selected from the group consisting of the nickel or indium chelate of iminodiacetic acid mixtures thereof.

27. The method in accordance with claim **22** wherein said metal chelate of an iminodiacetic acid is selected from the group consisting of the cobalt chelate of iminodiacetic acid, the zinc chelate of iminodiacetic acid, the cadmium chelate of iminodiacetic acid, and mixtures thereof.

28. An aqueous electrolytic bath for gold plating comprising a gold cyanide as a gold source in an amount to provide a gold concentration within the range of from about 1 to about 24 grams/liter, said gold cyanide comprising ammonium aurocyanide or potassium aurocyanide, a metal chelate of an iminodiacetic acid in an amount to provide a concentration of said metal within the range of from about 0.05 to about 10 grams/liter, said metal chelate of an iminodiacetic acid

comprising the nickel chelate of iminodiacetic acid, at least one conducting salt in an amount within the range of from about 10 to about 150 grams/liter, said conducting salt comprising ammonium or alkali metal sulfamate, and a buffer to maintain said electrolytic bath at a pH within the range of from about 3 to about 4.5, said buffer comprising aminoacetic acid in in an amount within the range of from about 5 to about 200 grams/liter, and further including the nickel chelate of ethylenediamine tetraacetic acid in an amount to provide a nickel concentration within the range of from about 0.25 to about 10 grams/liter.

29. The electrolytic bath in accordance wtih claim **28,** further including the indium chelate of ethylenediamine tetraacetic acid in an amount to provide an indium concentration within the range of from about 0.25 to about 15 grams/liter.

30. The electrolytic bath in accordance with claim **28,** further including the cobalt chelate of iminodiacetic acid in an amount to provide a cobalt concentration within the range of from about 0.05 to about 10 grams/liter.

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