

Modified Cyanide-Free Gold Plating Solution and Use Thereof, as well as Preparation Method for Hard Gold

Field of the Invention

The present invention relates to a modified cyanide-free gold plating solution, a use of the modified cyanide-free gold plating solution in preparation of a gold article, and a preparation method of hard gold.

Background of the Invention

As people's living standard is improved increasingly, gold articles are more and more favored by the consumers. Presently, there are more and more gold articles produced by electroplating. The plating solutions used in electroplating processes are mainly solutions that comprise potassium aurous cyanide. However, cyanide-containing plating solutions are highly toxic substances which bring harms to the physical health of the producers in the production process of the gold articles; in addition, it requires a high cost to treat the waste liquid produced in the production to reduce environmental pollution caused by the waste liquid.

To overcome the above-mentioned defects of the cyanide-containing plating solutions, in recent years, some companies replace solutions that comprise potassium aurous cyanide with solutions that comprise auric sulfite salts (auric potassium sulfite and/or auric sodium sulfite) as plating solution for preparing gold articles. However, owing to the poor stability of auric sulfite salts, gold may precipitate easily during the electroplating process, resulting in degraded stability of the electroplating process and degraded performance of the gold articles. Moreover, gold articles obtained by using a solution that comprises auric sulfite salt as the plating solution have low hardness; consequently, high-purity gold articles produced with such a solution, particularly pure gold, may have deformations and sags easily, and may be broken easily during use. In view of the above, in recent years, researchers have made some improvements to the plating solutions that contain auric sulfite salt in order to improve the hardness of gold articles. For example, the Chinese Patent No. CN103938232A has disclosed a cyanide-free gold plating solution and a preparation method thereof. The cyanide-free gold plating solution comprises an auric sulfite salt, a phosphate, a hydrophosphate, an alkali metal sulfite salt, an antimonite salt and/or a selenium salt, and a complexing agent. However, though the cyanide-free gold plating solution has higher stability and when the cyanide-free gold plating solution is used to produce a gold article, a gold article with higher hardness can be obtained, the gold article obtained from the cyanide-free gold plating solution has poor brightness. Therefore, further improvement is required.

Summary of the Invention

The object of the invention is to overcome the drawback that the stability of the existing cyanide-free gold plating solutions and the hardness and brightness of a gold article produced from the cyanide-free gold plating solutions can't be ensured at the same time, thereby providing a modified cyanide-free gold plating solution with higher stability, and a gold article with higher hardness and brightness can be obtained by using such solution; in addition, the present invention provides a use of the the modified cyanide-free gold plating solution in preparation of a gold article, and a preparation method of a hard gold.

Specifically, the present invention provides a modified cyanide-free gold plating solution, which comprises an auric sulfite salt, an organic phosphonate salt, a hydrophosphate mixed salt, an alkali metal sulfite salt, an antimonite salt, a selenium salt, a complexing agent, an organic polyamine based compound, and a polyether based compound.

The present invention also provides a use of the modified cyanide-free gold plating solution in preparation of a gold article.

Moreover, the present invention further provides a preparation method of a hard gold, which comprises: electroplating a gold layer on a mandrel made of a low-melting material, then forming holes that penetrate the electroplated layer to reach the mandrel, and melting the mandrel so that the mandrel material is discharged through the holes, wherein, the method of electroplating the gold layer on the mandrel comprises utilizing the mandrel as a cathode and electroplating it in the modified cyanide-free gold electroplating solution described above.

Through in-depth research, the inventors of the present invention found that: if the above-mentioned substances contained in the modified cyanide-free gold electroplating solution are used in combination, the stability of the auric sulfite salt liquid in the modified cyanide-free gold electroplating solution could not only be improved remarkably, so that the electroplating process can be executed smoothly and steadily, but also the hardness and surface brightness of the obtained gold articles can be improved, and the electrochemical performance of the gold articles (cyclic voltammetry curve) is substantially the same as that of a pure gold electrode; in addition, except for zinc, even if the waste plating solution produced in the electroplating process is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents. Therefore, the modified cyanide-free gold plating solution and the preparation method of hard gold utilizing the modified cyanide-free gold plating solution provided in the present invention have excellent prospects in industrial use.

Other features and advantages of the present invention will be further detailed in

the embodiments hereunder.

Brief Description of the Drawings

The accompanying drawings are provided to facilitate further understanding of the present invention, and constitute a part of the description. They are used together with the following embodiments to explain the present invention, but not to limit the present invention. In the figures:

Fig.1 shows a specific preparation method of gold article provided in the present invention.

Brief Description of the Symbols

10 - mandrel; 11 - silicone rubber mold; 12 - cleaning liquid; 13 - copper plating solution; 14 - gold plating solution; 15 - nickel plating solution; 20 - hanger

Detailed Description of the Embodiments

The embodiments of the present invention will be described in detail hereafter. It should be understood that the embodiments described here are only provided to describe and explain the present invention, but shall not be deemed as constituting any limitation to the present invention.

The modified cyanide-free gold plating solution provided in the present invention comprises an auric sulfite salt, an organic phosphonate salt, a hydrophosphate mixed salt, an alkali metal sulfite salt, an antimonite salt, a selenium salt, a complexing agent, an organic polyamine based compound, and a polyether based compound. Furthermore, the modified cyanide-free gold plating solution may be transported or sold in a form that comprises the above-mentioned substances; however, to meet the requirement of later use, the modified cyanide-free gold electroplating solution usually further comprises water.

Preferably, the amount of the auric sulfite salt is 17-21g/L, the amount of the organic phosphonate salt is 10-30g/L, the amount of the hydrophosphate mixed salt is 30-150g/L, the amount of the alkali metal sulfite salt is 30-120g/L, the total amount of the antimonite salt and the selenium salt is 0.01-2g/L, the amount of the complexing agent is 0.01-5g/L, the amount of the organic polyamine based compound is 1-5g/L, and the amount of the polyether based compound is 0.01-0.05g/L; more preferably, the amount of the auric sulfite salt is 18-20g/L, the amount of the organic phosphonate salt is 15-30g/L, the amount of the hydrophosphate mixed salt is 40-120g/L, the amount of the alkali metal sulfite salt is 40-100g/L, the total amount of the antimonite salt and the selenium salt is 0.5-1.5g/L, the amount of the complexing agent is 2-5g/L, the amount of the

organic polyamine based compound is 1-3g/L, and the amount of the polyether based compound is 0.01-0.03g/L. The remaining content in the modified cyanide-free gold plating solution usually is water.

In the cyanide-free gold plating solution, auric sulfite salt and alkali metal sulfite salt are main components, wherein, the former is used to provide gold, and the latter is used as a stabilizer; all other components are used as additive to attain better effects, such as electrical conduction, buffering, anti-oxidation reduction, and surface activity.

The auric sulfite salt may be various types of existing gold complex comprising a sulfite ligand, which is free of cyanide and can be used by electroplating to obtain a gold article. Examples of the auric sulfite salt include but not limited to at least one of auric potassium sulfite, auric sodium sulfite, and auric ammonium sulfite. However, in view that the auric ammonium sulfite may produce toxic ammonia gas in the electroplating process, the auric sulfite salt is particularly preferably auric potassium sulfite and/or auric sodium sulfite.

The organic phosphonate salt may be various types of salt compound that comprises phosphonate radicals ($-\text{PO}_2$). Owing to the fact that phosphonate radical has stronger coordination ability than phosphate, the C-P bond is very stable, and phosphonate radicals can work with the central gold atom to form a complex that has a three membered ring; thus, the stability of auric sodium sulfite can be improved. Particularly, substances that contain multiple phosphonate radicals, such as hydroxy ethylidene diphosphonic acid group, the O-P-C-P-O chain in the molecular structure is a W-shaped planar structure, in which the coordination number for gold ions is 2, can form a coordination configuration of a five membered ring, which has a remarkable stabilizing effects for auric sodium sulfite. Therefore, the organic phosphonate salt in the present invention preferably is a hydroxy ethylidene diphosphonate salt, more preferably is potassium salt of hydroxy ethylidene diphosphonic acid or sodium salt of hydroxy ethylidene diphosphonic acid.

The hydrophosphate mixed salt refers to a mixture of at least two types of hydrophosphates. The hydrophosphate may be various types of common water-soluble hydrophosphate in the art. It may be one or more of dihydric phosphates, or one or more of monohydric phosphates, or a mixture of them. In the case that the hydrophosphate is a mixture of monohydric phosphate and dihydric phosphate, preferably, the weight ratio of monohydric phosphate to dihydric phosphate is 0.8-1.2:2. For example, the water-soluble hydrophosphate may be one or more of dipotassium hydrogen phosphate, potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium dihydrogen phosphate. The hydrophosphate mixed salt preferably is selected from a mixture of dipotassium hydrogen phosphate and potassium dihydrogen phosphate and/or a mixture of disodium hydrogen phosphate and sodium dihydrogen phosphate,

wherein, further preferably the weight ratio of dipotassium hydrogen phosphate to potassium dihydrogen phosphate is 0.8-1.2:2, and preferably the weight ratio of disodium hydrogen phosphate to sodium dihydrogen phosphate is 0.8-1.2:2.

The alkali metal sulfite salt preferably is potassium sulfite and/or sodium sulfite.

In the modified cyanide-free gold electroplating solution provided in the present invention, the weight ratio of the antimonite salt to the selenium salt preferably is 0.25-1:1, more preferably 0.3-0.6:1. In the present invention, the antimonite salt refers to a salt substance that comprises antimony element, including but not limited to one or more of antimony tartrate salt, antimonate salt, and oxyacid antimony. Examples of the antimonite salt include but not limited to at least one of sodium antimony tartrate, potassium antimony tartrate, antimony acetate, potassium pyroantimonate, sodium pyroantimonate, sodium antimonate, and potassium antimonate. The selenium salt refers to a salt substance that contains selenium element, including, but not limited to one or more of selenosulfate salt and selenite salt. Examples of the selenium salt include but not limited to at least one of sodium selenosulfate, potassium selenosulfate, zinc selenite, sodium selenite, and potassium selenite.

The complexing agent may be various types of existing substance that can work with gold ions to form complex ions. For example, the complexing agent may be selected from at least one of citric acid, tartaric acid, sodium ethylene diamine tetraacetate, aminoacetic acid, thiourea, and sodium thiosulfate.

The organic polyamine based compound has a strong chelation effect to gold atoms, and can work with gold atoms to form a stable chelate. Besides, such a chelator has surface activity in itself, and often strengthens cathodic polarization owing to adsorption on the cathode; thus, a fine and bright gold plating layer can be obtained. The organic polyamine based compound may be any compound that comprises two or more amino groups, and the amino group may be one or more of primary amino, secondary amino, and tertiary amino; preferably, the organic polyamine based compound is one or more of C2-6 alkyl diamine and C2-6 polyethylene-polyamine; in the present invention, preferably the organic polyamine based compound is at least one of ethylene diamine, propylene diamine, ethoxyl ethylene diamine, triethylene diamine, diethylene triamine, tetraethylene pentamine, pentaethylene hexamine, and butane diamine. Particularly, the propylene diamine may work with the gold atoms in the auric sodium sulfite to form a chelate of a six membered ring structure that has lower steric hindrance, so as to strengthen the stability.

When an auric sulfite plating solution is used for gold plating, a polyether based compound belongs to a non-ionic surfactant, in which the molecular chain structure comprises $[R_1-O-R_2]_n$ groups (R_1 and R_2 are aliphatic carbon chains), which can be absorbed to the surface of the gold layer and diffused, wherein, the

oxygen atoms in the hydrophilic ether oxygen groups can react with the reduced gold atoms, and produce a strong oriented adsorption effect and thereby inhibit the electro-crystallization process, and control the rate of discharge. Thus, on the microscopic concave-convex surface of the gold layer, owing to the fact that the thickness of effective diffusion layer at valleys is greater than the thickness of effective diffusion layer at peaks, the diffusion velocity of polyether into the microscopic valleys is lower than the diffusion velocity of it into peaks. As a result, the current at peaks is lower than that at valleys, and the increase rate of plating layer at peaks is slower than that at valleys; thus, the peaks and valleys are levelled up and a leveling effect is attained. A direct result of such an effect is that the brightness of the gold layer is improved. The polyether based compound of the present invention may be any polymer that comprises $[R_1-O-R_2]_n$ groups, including, but not limited to one or more of propylene glycol block polyether, polyoxyethylene, and polysorbate, particularly preferably is propylene glycol block polyether. The number-average molecular weight of the polyether based compound preferably is 800-1,500. Wherein, examples of the designations of the propylene glycol block polyether include but not limited to at least one of polyether L35, polyether L44, polyether L45, polyether L64, polyether L65, polyether 1720, and polyether 1740, etc.

Furthermore, the present invention also provides a use of the above-mentioned modified cyanide-free gold electroplating solution in preparation of a gold article.

The main improvement in the present invention lies in employing a novel modified cyanide-free gold electroplating solution, while the specific method for forming the gold article may be the same as that in the prior art.

According to a preferred embodiment of the present invention, the preparation method of the gold article comprises: electroplating a gold layer on a mandrel made of a low-melting material, forming holes that penetrate the plated layer to reach the mandrel, and melting the mandrel so that the mandrel material is discharged through the holes, wherein, the method for electroplating the gold layer on the mandrel comprises utilizing the mandrel as a cathode and electroplating in the modified cyanide-free gold plating solution described above. In the process of electroplating gold on the mandrel, the anode material may be a conventional choice in the art. For example, the anode material may be at least one of Ir-Ti composite material, Ru-Ir-Ti composite material, and Pt-Ti composite material, wherein, the anode materials above are usually in a clad structure, in which the core layer is metallic titanium, and a thin layer adheres to the surface of the core layer are made of at least one of metallic iridium, metallic ruthenium, metallic iridium, and platinum etc.. The thickness of the thin layer usually is 2.5-5 μ m. Furthermore, the anode may exist in any shape in the prior art, particularly preferably a mesh shape, such as rhombic mesh shape, circular mesh shape, or square mesh shape, etc., so as to improve the penetrability of the

modified cyanide-free gold plating solution and facilitate successful electroplating of the gold layer.

The mandrel mainly takes a role of a mold for shaping so that the gold articles of different shapes shall be obtained; in addition, the gold article obtained after the mandrel is removed is in a hollow structure, and thereby the quantity of gold required for producing a gold article with the same volume can be saved. In the present invention, the "low melting" refers to that the melting point is not higher than 200°C, preferably is 60-180°C. The low-melting mandrel may be made of Sn-Bi alloy and/or wax. Wherein, in the case of a Sn-Bi alloy, the weight ratio of Sn to Bi may be 0.5-1.5:1. In the case that the low-melting mandrel is made of wax, usually electrical-conductive silver oil must be coated on the surface of the wax. Examples of the wax include but not limited to one or more of bee wax, mineral wax (e.g., lignite wax, ozokerite, paraffin), and petroleum wax, etc. The size and shape of the mandrel may be selected reasonably according to the size and shape of the gold article to be obtained which is omitted here.

Furthermore, owing to the fact that the mandrel may erode gold when the mandrel is melted and discharged at a high temperature, preferably a first copper layer is electroplated on the mandrel, and then the gold layer is electroplated on the first copper layer, next, a second copper layer and/or nickel layer is electroplated, so as to attain a protective effect and prevent erosion of the gold layer when the mandrel is melted and discharged. Furthermore, after the mandrel is melted and discharged, preferably the first copper layer, the second copper layer and/or the nickel layer, and the residual mandrel material are removed with nitric acid, so that only a hollow three-dimensional gold layer, i.e., the required gold article is kept.

According to the present invention, when the gold layer is electroplated on the mandrel or the first copper layer, the electroplating conditions usually may include: temperature of the electroplating solution: 40-60°C, pH of the electroplating solution: 6-8, cathode current density: 0.1-1A/dm², and electroplating time: 8-20h. Furthermore, the thickness of the formed gold layer may be 150-250µm, preferably is 160-230µm. The method for controlling the pH of the electroplating solution within the above-mentioned range is well known to those skilled in the art. For example, an acidic substances or alkaline substances may be added into the electroplating solution. For example, the acidic substances may be one or more of sulfuric acid, phosphoric acid, and propandioic acid, etc. For example, the alkaline substances may be one or more of sodium hydroxide, potassium hydroxide, sodium sulfite, and potassium sulfite, etc. The acidic substances and the alkaline substances may be dosed in an appropriate quantity so that the pH of the electroplating solution is adjusted to the above-mentioned range which is omitted here.

In the specific preparation process of the hard gold, the method for forming the first copper layer usually comprises utilizing the low-melting material (e.g., Sn-Bi alloy and/or wax; in the case of wax, usually electrical-conductive silver oil must be coated on the surface of the wax) as an cathode, utilizing phosphorus copper as a an anode, and electroplating in the electroplating solution that comprises copper sulfate. The method for forming the second copper layer usually comprises utilizing the product plated with a gold layer as a cathode, utilizing a phosphorus copper as an anode, and electroplating in the electroplating solution that comprises acidic copper sulfate. The electroplating solutions that contain acidic copper sulfate in the former two copper plating procedures may be conventional choices in the art, which are well known to those skilled in the art, and will not be further detailed here.

The electroplating conditions for forming the first copper layer may be the same as or different from the electroplating conditions for forming the second copper layer, and may each independently include: temperature of electroplating solution: 15-35°C, pH of electroplating solution: 0.1-0.5, cathode current density: 0.5-5A/dm², electroplating time: 30-60min. Furthermore, the thickness of the formed first copper layer may be 15-80μm, preferably is 30-60μm; the thickness of the formed second copper layer may be 30-60μm, preferably is 45-55μm. The first copper layer preferably is bright and smooth, so that the gold layer obtained subsequently is bright and smooth.

According to the present invention, the method for forming the nickel layer usually comprises utilizing the product selectively electroplated with the second copper layer as a cathode, utilizing pure metallic nickel as an anode, and electroplating in a nickel plating solution. The kind of the nickel plating solution may be a conventional choice in the art, and is well known to those skilled in the art, which will not be further detailed here. The electroplating conditions for forming the nickel layer usually include: temperature of electroplating solution: 35-50°C, pH of electroplating solution: 3.5-5, cathode current density: 2-4A/dm², and electroplating time: 10-20min. Furthermore, the thickness of the formed nickel layer may be 5-20μm, preferably is 5-10μm.

Furthermore, the residual low-melting material as well as the first copper layer, the second copper layer and/or the nickel layer may be removed with any existing method in the prior art. For example, after the mandrel is removed, the obtained preformed gold article may be immersed in a hot concentrated nitric acid solution and treated at 80-100°C temperature.

According to one embodiment of the present invention, as shown in Fig. 1, the preparation method of hard gold comprises: casting a mandrel 10 made of a low-melting alloy by centrifugal casting in a silicone rubber mold 11, loading the mandrel 10 into a rotary drum to remove burrs and any parting line, and then

connecting the mandrel 10 to a hanger 20 of a plating rack, and cleaning the mandrel 10 in an electrolytic and/or ultrasonic cleaning liquid 12. If the melting point of the mandrel 10 is lower than the temperature of the electroplating solution that is used to form the gold layer, a first copper layer must be formed on the mandrel 10, i.e., the cleaned mandrel 10 is transferred to a copper plating solution 13 and then plating is carried out, to form a first copper layer on the surface of the mandrel 10. The first copper layer should be bright and smooth, so that the gold layer formed subsequently is bright and smooth. The mandrel 10 electroplated with the first copper layer is placed in a gold plating solution 14 and electroplated to form a gold layer, and then obtained part is placed in the copper plating solution 13 and plated to form a second copper layer on the gold layer. After the second copper layer is formed, the obtained part is placed in a nickel plating solution 15 and electroplated to form a nickel layer on the second copper layer. After the electroplating is finished, the obtain part is removed from the hanger 20, and two or more holes that penetrate through the plated layers to reach the center of the mandrel 10 are drilled out at appropriate positions on the part. Then, the part is loaded into an oven and heated up to about 200 °C, so that the low-melting mandrel 10 is melted and flows out through the holes. Next, after the low-melting mandrel 10 is removed, the part is immersed in a concentrated nitric acid solution to remove residual low-melting material and the first copper layer, the second copper layer, and the nickel layer, and only the gold layer is kept; thus, a gold article is obtained.

Each of the above electroplating steps may be executed in the conventional way. For example, the part that includes the mandrel 10 and the associated metal layers formed subsequently may be electrically connected to a negative pole of a DC power source via the hanger 20 and inserted into a corresponding electroplating solution, while the anode may be connected to the positive pole of the DC power source and inserted into the corresponding electroplating solution.

Furthermore, the preparation method of the hard gold further comprises after the residual low-melting material, the first copper layer, the second copper layer and/or the nickel layer are removed from the hard gold, processing the gold article by soldering, sand blasting, and polishing, etc. to turn it into a jewelry product.

Hereunder the present invention will be detailed in embodiments.

In the preparation process of the gold article, the anode material used in the gold plating procedure is an Ir-Ti composite material in a rhombic mesh structure, which consists of a metallic titanium core layer and a metallic iridium layer that adheres to the metallic titanium core layer, wherein, the cross section of the metallic titanium core layer is a 1mm×0.5mm rectangle, the average thickness of the metallic iridium layer (manufacturer: Guangzhou Great Wall Titanium Metal

Co., Ltd.) is 5 μ m, the side length of the rhombi in the Ir-Ti composite material of rhombic mesh structure is 10mm, and the acute included angle between the sides is 60°; the anode material used in the copper plating procedure is a cylindrical P-Cu composite material (made by homogeneously mixing 99.94wt% copper and 0.06wt% phosphorus, at 8.89g/cm³ density), in dimensions of 25mm (radius of base circle) $\times$ 30mm (height of cylinder); the anode material used in the nickel plating procedure is cylindrical metallic nickel, in dimensions of 25mm (radius of base circle) $\times$ 30mm (height of cylinder).

The stability and cathode current efficiency of the modified cyanide-free gold plating solution are tested using a cathode current efficiency method, as follows: a copper sulfate electroplating solution consisting of copper sulfate, sulfuric acid, ethanol and water is prepared, wherein, the concentration of copper sulfate is 125g/L, the concentration of sulfuric acid is 25ml/L, and the concentration of ethanol is 50ml/L; then, the copper sulfate electroplating solution (1,000mL) and the modified cyanide-free gold plating solution (1,000mL) are loaded into a plating tank a (in dimensions of 120mm (L) $\times$ 120mm (W) $\times$ 100mm (H)) and a plating tank b (in dimensions of 120mm (L) $\times$ 120mm (W) $\times$ 100mm (H)) respectively, a phosphorus copper plate (made by mixing homogeneously and pressing 99.94wt% copper and 0.06wt% phosphorus, at 8.89g/cm³ density, in dimensions of 80mm (L) $\times$ 60mm (W) $\times$ 3mm (T)) is inserted in the plating tank a and used as an anode (marked as anode a), the Ir-Ti composite material of rhombic mesh structure (consisting of a metallic titanium core layer and a metallic iridium layer adhering to the metallic titanium core layer, the average thickness of the metallic iridium layer is 3 μ m, the side length of the rhombi of Ir-Ti composite material in a rhombic mesh structure is 10mm, the acute included angle between the sides is 60°) is inserted in the plating tank b and used as an anode (marked as anode b), an cathode test piece a (a pure copper plate, in dimensions of 25mm (L) $\times$ 25mm (W) $\times$ 0.3mm (T)) and a cathode test piece b (a pure copper plate, in dimensions of 25mm (L) $\times$ 25mm (W) $\times$ 0.3mm (T)) are cleaned and weighed, and then the cathode test piece a is inserted into the plating tank a, and the cathode test piece b is inserted into the plating tank b; then, the anode a is connected to the positive pole of a power supply through a conductive wire, the cathode test piece a is connected to the anode b through a conductive wire, the cathode test piece b is connected to the negative pole of the power supply unit through a conductive wire, and then power is applied, and plating is carried out at 0.03A constant current for 10min., wherein, the operating temperature in the electroplating tank a is 25°C, the operating temperature in the plating tank b is 60°C; after the plating is finished, the cathode test piece a and the cathode test piece b are taken out, cleaned, dried, and weighed, and then the cathode current efficiency is calculated according to the following formula:

$\eta = 0.165 \times \Delta Ma / \Delta Mb \times 100\%$ (η : cathode current efficiency, ΔMa : increased weight of the cathode test piece a, ΔMb : increased weight of the cathode test piece b); if the cathode current efficiency is 90% or higher, it indicates that the stability of the cyanide-free gold electroplating solution is high; if the cathode current efficiency is 85% or lower, it indicates that the stability of the cyanide-free gold electroplating solution is low.

The surface brightness of the gold article is judged with the following method: an unpolished copper plate is electroplated continuously for 4h with corresponding modified cyanide-free gold electroplating solution to form a plated gold layer on the copper plate, and then the brightness and smoothness of the plated gold layer are checked visually. From bottom to top, the brightness levels include: matte, semi-gloss, gloss, high gloss, and mirror gloss.

Preparation example 1

This preparation example is provided to describe the modified cyanide-free gold plating solution and the preparation method thereof provided in the present invention.

19g auric sodium sulfite, 16g sodium hydroxyethylidene diphosphonic acid, 20g disodium hydrogen phosphate, 40g sodium dihydrogen phosphate, 50g sodium sulfite, 0.2g sodium antimony tartrate, 0.4g sodium selenite, 2g aminoacetic acid, 2g propylene diamine, and 0.01g polyether L35 are dissolved in 1L water at 60 °C, to obtain a modified cyanide-free gold plating solution Z1. The stability and cathode current efficiency of the modified cyanide-free gold plating solution Z1 are measured with a cathode current efficiency method. The result indicates that the modified cyanide-free gold plating solution Z1 has high stability, and the cathode current efficiency is 93% or higher.

Preparation example 2

This preparation example is provided to describe the modified cyanide-free gold plating solution and the preparation method thereof provided in the present invention.

19g auric sodium sulfite, 24g sodium hydroxyethylidene diphosphonic acid, 40g disodium hydrogen phosphate, 80g sodium dihydrogen phosphate, 80g sodium sulfite, 0.4g potassium antimony tartrate, 0.8g sodium selenosulfate, 5g aminoacetic acid, 5g ethylene diamine, and 0.03g polyether L35 are dissolved in 1L water at 60 °C, to obtain a modified cyanide-free gold plating solution Z2. The stability and cathode current efficiency of the modified cyanide-free gold plating solution Z2 are tested according to the method described in the preparation

example 1. The result indicates that the modified cyanide-free gold plating solution Z2 has high stability, and the cathode current efficiency is 93% or higher.

Preparation example 3

This preparation example is provided to describe the modified cyanide-free gold electroplating solution and the preparation method of the modified cyanide-free gold electroplating solution provided in the present invention.

19g auric sodium sulfite, 20g sodium hydroxyethylidene diphosphonic acid, 30g disodium hydrogen phosphate, 60g sodium dihydrogen phosphate, 60g sodium sulfite, 0.3g sodium antimonate, 0.6g sodium selenite, 3g aminoacetic acid, 4g butane diamine, and 0.02g polyether L35 are dissolved in 1L water at 60 °C, to obtain a modified cyanide-free gold plating solution Z3. The stability and cathode current efficiency of the modified cyanide-free gold plating solution Z3 are tested according to the method described in the preparation example 1. The result indicates that the modified cyanide-free gold plating solution Z3 has very high stability, and the cathode current efficiency is 95% or higher.

Preparation example 4

This preparation example is provided to describe the modified cyanide-free gold electroplating solution and the preparation method thereof provided in the present invention.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 1, but the dose of the sodium antimony tartrate is 0.01g, and the dose of the sodium selenite is 0.015g; thus, a modified cyanide-free gold plating solution Z4 is obtained. The stability and cathode current efficiency of the modified cyanide-free gold plating solution Z4 are tested according to the method described in the preparation example 1. The result indicates that the modified cyanide-free gold plating solution Z4 has high stability, and the cathode current efficiency is 90% or higher.

Preparation example 5

This preparation example is provided to describe the modified cyanide-free gold plating solution and the preparation method thereof provided in the present invention.

19g auric sodium sulfite, 20g disodium 1-hydroxypropylidene-1,1-diphosphonic acid, 24g disodium hydrogen phosphate, 60g sodium dihydrogen phosphate, 60g sodium sulfite, 0.3g sodium antimonate, 0.6g sodium selenite, 3g aminoacetic acid, 4g tetraethylene pentamine, and 0.02g polyether L1720 are dissolved in 1L

water at 30°C, to obtain a modified cyanide-free gold plating solution Z5. The stability and cathode current efficiency of the modified cyanide-free gold plating solution Z5 are tested according to the method described in the preparation example 1. The result indicates that the modified cyanide-free gold plating solution Z5 has very high stability, and the cathode current efficiency is 95% or higher.

Comparative preparation example 1

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 4, but the sodium hydroxyethylidene diphosphonic acid is not added; thus, a reference modified cyanide-free gold plating solution DZ1 is obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ1 are tested according to the method described in the preparation example 1. The result indicates that the reference modified cyanide-free gold plating solution DZ1 has low stability, and the cathode current efficiency is only 80% at the most.

Comparative preparation example 2

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 4, but the hydrophosphate mixed salt is not added (i.e., the disodium hydrogen phosphate and the sodium dihydrogen phosphate are not added); thus, a reference modified cyanide-free gold plating solution DZ2 is obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ2 are tested according to the method described in the preparation example 1. The result indicates that the reference modified cyanide-free gold plating solution DZ2 has low stability, and the cathode current efficiency is only 80%.

Comparative preparation example 3

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the comparative preparation example 1, but the aminoacetic acid is not added; thus, a reference modified cyanide-free gold plating solution DZ3 is

obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ3 are tested according to the method described in the preparation example 1. The result indicates that the reference modified cyanide-free gold plating solution DZ3 has low stability, and the cathode current efficiency is only 85%.

Comparative preparation example 4

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 2, but the propylene diamine and the polyether L35 are not added; thus, a reference modified cyanide-free gold plating solution DZ4 is obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ4 are tested according to the method described in the preparation example 2. The result indicates that the reference modified cyanide-free gold plating solution DZ4 has relatively low stability, and the cathode current efficiency is only 88%.

Comparative preparation example 5

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 2, but the polyether L35 is not added; thus, a reference modified cyanide-free gold plating solution DZ5 is obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ5 are tested according to the method described in the preparation example 2. The result indicates that the reference modified cyanide-free gold plating solution DZ5 has relatively low stability, and the cathode current efficiency is only 89%.

Comparative preparation example 6

This comparative preparation example is provided to describe a reference modified cyanide-free gold plating solution and a preparation method thereof.

A modified cyanide-free gold plating solution is prepared with the method described in the preparation example 2, but the propylene diamine is not added; thus, a reference modified cyanide-free gold plating solution DZ6 is obtained. The stability and cathode current efficiency of the reference modified cyanide-free gold plating solution DZ6 are tested according to the method

described in the preparation example 2. The result indicates that the reference modified cyanide-free gold plating solution DZ6 has relatively low stability, and the cathode current efficiency is only 89%.

Example 1

This example is provided to describe the preparation method of a gold article provided in the present invention.

As shown in Fig. 1, a mandrel 10 made of a low-melting Sn-Bi alloy (the weight ratio of Sn to Bi is 42:58, the same below) is cast in a silicone rubber mold 11 by centrifugal casting (the radius of centrifugation is 10cm, and the rotation speed is 900r/min.), the mandrel 10 is loaded into a rotary drum to remove burrs or any parting line, and then the mandrel 10 is connected to a hanger 20 of a plating rack, and is cleaned in an ultrasonic cleaning liquid 12. Next, the cleaned mandrel 10 is transferred into a copper plating solution 13 (a plating solution mainly consisting of 200g/L copper sulfate and 70g/L sulfuric acid, the same below) and is electroplated, wherein, the electroplating conditions include that: temperature of the copper plating solution 13: 25°C, pH of the copper electroplating solution 13: 0.1, cathode current density: 4A/dm², electroplating time: 1h; thus, a first copper layer in thickness of 50μm is formed. Then, the mandrel 10 plated with the first copper layer is immersed in a gold plating solution 14 (the modified cyanide-free gold plating solution Z1) and electroplated, wherein, the electroplating conditions include: temperature of the modified cyanide-free gold plating solution Z1: 60°C, pH of the modified cyanide-free gold plating solution Z1: 7.2, cathode current density: 0.45A/dm², and electroplating time: 10h; thus, a gold layer in thickness of 170μm is formed. Next, the part plated with the gold layer is immersed in a copper plating solution 13 and electroplated, wherein, the electroplating conditions include: temperature of the copper electroplating solution 13: 25°C, pH of the copper electroplating solution 13: 0.1, cathode current density: 4A/dm², and electroplating time: 1h; thus, a second copper layer in thickness of 50μm is formed. Then, the part plated with the second copper layer is immersed in a nickel plating solution 15 (a plating solution mainly consisting of 20g/L boric acid, 100g/L nickel chloride and 100g/L nickel sulfate, the same below) and plated, wherein, the electroplating conditions include: temperature of the nickel plating solution 15: 45°C, pH of the nickel plating solution 15: 4, cathode current density: 2A/dm², and electroplating time: 20min.; thus, a nickel layer in thickness of 10μm is formed. After the electroplating is finished, the obtain part is removed from the hanger 20, and two or more holes that penetrate through the plated layers to the center of the mandrel 10 are drilled out at appropriate positions on the part. Then, the part is loaded into an oven and heated up to about 200°C, so that the low-melting mandrel 10 is melted and flows out through the holes. Next,

after the low-melting mandrel 10 is removed, the part is immersed in a concentrated nitric acid solution to remove residual low-melting material and the first copper layer, the second copper layer, and the nickel layer, a gold article only with the gold layer is obtained. Tested with a Vickers hardness tester (Model YN21125HR-150 bought from Suzhou Ulux Instrument Co., Ltd., the same below), the hardness of the gold article is 132Hv, the gold purity tested by pyrognostic test is 99.95%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste plating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 2

This example is provided to describe the preparation method of a gold article provided in the present invention.

As shown in Fig. 1, a mandrel 10 made of a low-melting Sn-Bi alloy is cast by centrifugal casting in a silicone rubber mold 11, then the mandrel 10 is loaded into a rotary drum to remove burrs and any parting line, and then the mandrel 10 is connected to a hanger 20 in a plating rack, and the mandrel 10 is cleaned in an ultrasonic cleaning liquid 12. Next, the cleaned mandrel 10 is transferred into a copper plating solution 13 and is electroplated, wherein, the electroplating conditions include: temperature of the copper plating solution 13: 25°C, pH of the copper plating solution 13: 0.1, cathode current density: 4A/dm², electroplating time: 1h; thus, a first copper layer in thickness of 50μm is formed. Then, the mandrel 10 plated with the first copper layer is immersed in a gold plating solution 14 (the modified cyanide-free gold plating solution Z2) and plated, wherein, the electroplating conditions include: temperature of the modified cyanide-free gold plating solution Z2: 60°C, pH of the modified cyanide-free gold plating solution Z2: 7.2, cathode current density: 0.45A/dm², and electroplating time: 10h; thus, a gold layer in thickness of 170μm is formed. Next, the part electroplated with the gold layer is immersed in a copper plating solution 13 and electroplated, wherein, the electroplating conditions include: temperature of the copper plating solution 13: 25°C, pH of the copper plating solution 13: 0.1, cathode current density: 4A/dm², and electroplating time: 1h; thus, a second copper layer in thickness of 50μm is formed. Then, the part plated with the second copper layer is immersed in a nickel plating solution 15 and electroplated, wherein, the electroplating conditions include: temperature of the nickel plating solution 15: 45°C, pH of the nickel plating solution 15: 4, cathode current density:

2A/dm², and electroplating time: 20min.; thus, a nickel layer in thickness of 10μm is formed. After the plating is finished, the obtained part is removed from the hanger 20, and two or more holes that penetrate through the plated layers to reach the center of the mandrel 10 are drilled out at appropriate positions on the part. Then, the part is loaded into an oven and heated up to about 200°C, so that the low-melting mandrel 10 is melted and flows out through the holes. Next, after the low-melting mandrel 10 is removed, the part is immersed in a concentrated nitric acid solution to remove residual low-melting material and the first copper layer, the second copper layer, and the nickel layer, thus, a gold article only with the gold layer is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 136Hv, the gold purity tested by pyrognostic test is 99.95%, the surface of the gold article is smooth, and the surface brightness level is High Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste electroplating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 3

This example is provided to describe the preparation method of a gold article provided in the present invention.

As shown in Fig. 1, a mandrel 10 made of a low-melting Sn-Bi alloy is cast by centrifugal casting in a silicone rubber mold 11, then the mandrel 10 is loaded into a rotary drum to remove burrs and any parting line, and then the mandrel 10 is connected to a hanger 20 of a plating rack, and the mandrel 10 is cleaned in an ultrasonic cleaning liquid 12. Next, the cleaned mandrel 10 is transferred into a copper electroplating solution 13 and electroplated, wherein, the electroplating conditions include: temperature of the copper plating solution 13: 25°C, pH of the copper plating solution 13: 0.1, cathode current density: 4A/dm², electroplating time: 1h; thus, a first copper layer in thickness of 50μm is formed. Then, the mandrel 10 plated with the first copper layer is immersed in a gold plating solution 14 (the modified cyanide-free gold plating solution Z3) and electroplated, wherein, the electroplating conditions include: temperature of the modified cyanide-free gold plating solution Z3: 60°C, pH of the modified cyanide-free gold plating solution Z3: 7.2, cathode current density: 0.45A/dm², and electroplating time: 10h; thus, a gold layer in thickness of 170μm is formed. Next, the part plated with the gold layer is immersed in a copper plating solution 13 and plated, wherein, the electroplating conditions include: temperature of the copper plating solution 13: 25°C, pH of the copper plating solution 13: 0.1, cathode

current density: 4A/dm^2 , and electroplating time: 1h; thus, a second copper layer in thickness of $50\mu\text{m}$ is formed. Then, the part plated with the second copper layer is immersed in a nickel plating solution 15 and electroplated, wherein, the electroplating conditions include: temperature of the nickel plating solution 15: 45°C , pH of the nickel plating solution 15: 4, cathode current density: 2A/dm^2 , and electroplating time: 20min.; thus, a nickel layer in thickness of $10\mu\text{m}$ is formed. After the plating is finished, the obtain part is removed from the hanger 20, and two or more holes that penetrate through the plated layers to the center of the mandrel 10 are drilled out at appropriate positions on the part. Then, the part is loaded into an oven and heated up to about 200°C , so that the low-melting mandrel 10 is melted down and flows out through the holes. Next, after the low-melting mandrel 10 is removed, the part is immersed in a concentrated nitric acid solution to remove residual low-melting material and the first copper layer, the second copper layer, and the nickel layer; thus, a gold article with only the gold layer is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 145Hv, the gold purity tested by pyrognostic test is 99.96%, the surface of the gold article is smooth, and the surface brightness level is Mirror Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste electroplating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 4

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 1, but in the gold electroplating procedure, the modified cyanide-free gold plating solution Z1 is replaced with the modified cyanide-free gold plating solution Z4; thus, a gold article in which only the gold layer is kept is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 100Hv, the gold purity tested by pyrognostic test is 99.92%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste electroplating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 5

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 4, but in the preparation process, the modified cyanide-free gold electroplating solution Z4 is used at 45°C temperature; thus, a gold article in which only the gold layer is kept is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 120Hv, the gold purity tested by pyrognostic test is 99.94%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste plating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 6

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 4, but the low-melting Sn-Bi alloy is replaced with paraffin in the same volume (the paraffin is coated with electrical-conductive silver oil) when the mandrel 10 is formed, and the modified cyanide-free gold plating solution Z4 is used at 45°C temperature; thus, a gold article is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 110Hv, the gold purity tested by pyrognostic test is 99.93%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. Except for zinc, even if the waste plating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Example 7

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 1, but in the gold plating procedure, the modified cyanide-free gold plating solution Z1 is replaced

with the modified cyanide-free gold plating solution Z5; thus, a gold article in which only the gold layer is kept is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 100Hv, the gold purity tested by pyrognostic test is 99.92%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification. In addition, the electrochemical performance (cyclic voltammetry curve) of the gold article is substantially the same as that of a pure gold electrode. except for zinc, even if the waste plating solution is directly discharged without treatment, it still substantially meets the indicators specified in the national standard "Special Discharge Limits of Water Pollutants" for electroplating effluents.

Comparative example 1

This comparative example is provided to describe a preparation method of a reference gold article.

Hard gold is prepared with the method described in the example 4, but in the gold layer electroplating procedure, the modified cyanide-free gold electroplating solution Z4 is replaced with the modified cyanide-free gold electroplating solution DZ1. Tested with a Vickers hardness tester, the hardness of the gold article obtained with this method is only 88Hv, the gold purity tested by pyrognostic test is 98.90%, the surface of the gold article is not smooth, and the surface brightness level is Semi-Gloss, inferior to the product specification.

Comparative example 2

This comparative example is provided to describe a preparation method of a reference gold article.

Hard gold is prepared with the method described in the example 4, but in the gold layer electroplating procedure, the modified cyanide-free gold plating solution Z4 is replaced with the modified cyanide-free gold plating solution DZ2. Tested with a Vickers hardness tester, the hardness of the gold article obtained with this method is only 75Hv, the gold purity tested by pyrognostic test is 98.80%, the surface of the gold article is not smooth, and the surface brightness level is Semi-Gloss, inferior to the product specification.

Comparative example 3

This comparative example is provided to describe a preparation method of a reference gold article.

Hard gold is prepared with the method described in the example 1, but in the gold layer electroplating procedure, the modified cyanide-free gold plating solution Z1

is replaced with the modified cyanide-free gold plating solution DZ3. Tested with a Vickers hardness tester, the hardness of the gold article obtained with this method is only 68Hv, the gold purity tested by pyrognostic test is 98.50%, the surface of the gold article is rough, and the surface brightness level is Semi-Gloss, inferior to the product specification.

Comparative example 4

This comparative example is provided to describe a preparation method of a reference gold article.

Hard gold is prepared with the method described in the example 2, but in the gold layer electroplating procedure, the modified cyanide-free gold plating solution Z2 is replaced with the modified cyanide-free gold plating solution DZ4. Tested with a Vickers hardness tester, the hardness of the gold article obtained with this method is only 85Hv, the gold purity tested by pyrognostic test is 99.91%, the surface of the gold article is smooth, and the surface brightness level is Semi-Gloss, inferior to the product specification.

Comparative example 5

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 1, but in the gold layer electroplating procedure, the modified cyanide-free gold plating solution Z1 is replaced with the modified cyanide-free gold plating solution DZ5; thus, a gold article in which only the gold layer is kept is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 100Hv, the gold purity tested by pyrognostic test is 99.92%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification.

Comparative example 6

This example is provided to describe the preparation method of a gold article provided in the present invention.

Hard gold is prepared with the method described in the example 1, but in the gold layer electroplating procedure, the modified cyanide-free gold plating solution Z1 is replaced with the modified cyanide-free gold plating solution DZ6; thus, a gold article in which only the gold layer is kept is obtained. Tested with a Vickers hardness tester, the hardness of the gold article is 100Hv, the gold purity tested by pyrognostic test is 99.92%, the surface of the gold article is smooth, and the surface brightness level is Gloss, in line with the product specification.

It could be found from the above results: the modified cyanide-free gold plating solution provided in the present invention has high stability, and the gold article obtained with the modified cyanide-free gold plating solution has higher hardness and higher surface brightness, and has excellent prospects of industrial application.

While some preferred examples of the present invention are described above, the present invention is not limited to the details in those examples. Within the range of the technical design of the present invention, various kinds of modifications could be made to the technical scheme of the present invention, without departing from the spirit of the present invention. However, all these modifications and variations shall be deemed as falling into the scope of protection of the present invention.

In addition, it should be appreciated that the each specific technical features described in the above embodiments can be combined in any appropriate manner, provided that there is no conflict among the technical features in the combination. To avoid unnecessary iteration, such possible combinations are not described here in the present invention.

Moreover, different embodiments of the present invention can be combined freely as required, as long as the combinations don't deviate from the ideal and spirit of the present invention. Such combinations shall also be deemed as falling into the scope disclosed in the present invention.

Claims

1. A modified cyanide-free gold plating solution, characterized in that, the modified cyanide-free gold plating solution comprises an auric sulfite salt, an organic phosphonate salt, a hydrophosphate mixed salt, an alkali metal sulfite salt, an antimonite salt, a selenium salt and a complexing agent, an organic polyamine based compound, and a polyether based compound; wherein

the concentration of the organic polyamine based compound is 1-5g/L, and the concentration of the polyether based compound is 0.01-0.05g/L.

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2. The modified cyanide-free gold plating solution according to claim 1, wherein, the concentration of the auric sulfite salt is 17-21g/L, the concentration of the organic phosphonate salt is 10-30g/L, the concentration of the hydrophosphate mixed salt is 30-150g/L, the concentration of the alkali metal sulfite salt is 30-120g/L, the total concentration of the antimonite salt and the selenium salt is 0.01-2g/L, the concentration of the complexing agent is 0.01-5g/L; preferably

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the concentration of the auric sulfite salt is 18-20g/L, the concentration of the organic phosphonate salt is 15-30g/L, the concentration of the hydrophosphate mixed salt is 40-120g/L, the concentration of the alkali metal sulfite salt is 40-100g/L, the total concentration of the antimonite salt and the selenium salt is 0.5-1.5g/L, the concentration of the complexing agent is 2-5g/L, the concentration of the organic polyamine based compound is 1-3g/L, and the concentration of the polyether based compound is 0.01-0.03g/L.

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3. The modified cyanide-free gold plating solution according to claim 1 or 2, wherein, the auric sulfite salt is auric potassium sulfite and/or auric sodium sulfite, the organic phosphonate salt is potassium hydroxy ethylidene diphosphonate and/or sodium hydroxy ethylidene diphosphonate; the hydrophosphate mixed salt is a mixture of dipotassium hydrogen phosphate and potassium dihydrogen phosphate and/or a mixture of disodium hydrogen phosphate and sodium dihydrogen phosphate; the alkali metal sulfite salt is potassium sulfite and/or sodium sulfite; preferably

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the hydrophosphate mixed salt is monohydric phosphate and dihydric phosphate; more preferably

the weight ratio of the monohydric phosphate to the dihydric phosphate is 0.8-1.2:2.

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4. The modified cyanide-free gold plating solution according to any one of claims 1-3, wherein, the weight ratio of the antimonite salt to the selenium salt is 0.25-1:1.
5. The modified cyanide-free gold plating solution according to any one of claims 1-4, wherein, the antimonite salt is selected from at least one of sodium antimony tartrate, potassium antimony tartrate, sodium antimonate, and potassium antimonate; the selenium salt is selected from at least one of sodium selenosulfate, potassium selenosulfate, sodium selenite, and potassium selenite.
6. The modified cyanide-free gold plating solution according to any one of claims 1-5, wherein, the complexing agent is selected from at least one of sodium ethylene diamine tetraacetate, aminoacetic acid, thiourea, and sodium thiosulfate.
7. The modified cyanide-free gold plating solution according to any of claims 1-6, wherein, the organic polyamine based compound is selected from at least one of ethylene diamine, propylene diamine, and butane diamine.
8. The modified cyanide-free gold plating solution according to any one of claims 1-7, wherein, the polyether based compound is propylene glycol block polyether.
9. Use of the modified cyanide-free gold plating solution of any one of claims 1-8 in preparation of a gold article.
10. A preparation method of hard gold, comprising: electroplating a gold layer on a mandrel made of a low-melting material, then forming holes that penetrate through the plated layer to reach the mandrel, and melting the mandrel so that the mandrel material is discharged through the holes, wherein, the method for electroplating the gold layer on the mandrel comprises utilizing the mandrel as a cathode and electroplating in the modified cyanide-free gold plating solution of any one of claims 1-8.
11. The method according to claim 10, wherein, the electroplating conditions include: the electroplating solution temperature of 40-60°C, the electroplating

solution pH 6-8, cathode current density of $0.1-1\text{A}/\text{cm}^2$, and electroplating time of 8-20h.

12. The method according to claim 10 or 11, wherein, the low-melting material is Sn-Bi alloy and/or wax.
13. The method according to any one of claims 10-12, wherein, the method further comprising: before electroplating the gold layer on the mandrel, electroplating a first copper layer on the mandrel, then electroplating the gold layer on the first copper layer, and then electroplating a second copper layer and/or a nickel layer.
14. The method according to claim 13, wherein, the thickness of the first copper layer is $15-80\mu\text{m}$, the thickness of the gold layer is $150-250\mu\text{m}$, the thickness of the second copper layer is $30-60\mu\text{m}$ and/or the thickness of the nickel layer is $5-20\mu\text{m}$.