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(71) Applicant: **ENTHONE-OMI, Inc.**

West Haven, Connecticut 06516 (US)

(72) Inventors:

- **Dimpre, Stéphanie**
94300 Vincennes (FR)

- **Marcus, Philippe, Ecole nat. sup. de chimie Paris**
75231 Paris Cedex 05 (FR)

- **Lalanne, Pierre**
01170 Echenevex (FR)

- **Biau, Jacques**
93340 Le Raincy (FR)

(74) Representative: **Kügele, Bernhard et al**

NOVAPAT INTERNATIONAL SA,
9, Rue du Valais
1202 Genève (CH)

(54) **Method of producing AuCuGa alloy coating using electrolysis, and alloys produced by such a method**

(57) The present invention relates to a method of producing a gold-copper-gallium (AuCuGa) alloy coating by electrodeposition on a substrate (2), using an aqueous electrolytic bath. The method is characterized in that the aqueous electrolytic bath comprises potassium aurocyanide ($\text{KAu}(\text{CN})_2$), copper cyanide (CuCN), potassium cyanide (KCN) or sodium cyanide (NaCN), and a gallium salt (e.g. gallium sulfate $\text{Ga}_2(\text{SO}_4)_3$). In particular, the molar concentration of gold cations ($[\text{Au}^+]$), copper cations ($[\text{Cu}^+]$) and gallium cations

($[\text{Ga}^{3+}]$) in the electrolytic bath is respectively comprised within the following ranges: $0,19 \text{ g/l} \leq [\text{Au}^+] \leq 2,17 \text{ g/l}$ ($0,1 \cdot 10^{-2} \text{ mol/l} \leq [\text{Au}^+] \leq 1,1 \cdot 10^{-2} \text{ mol/l}$); $0,31 \text{ g/l} \leq [\text{Cu}^+] \leq 1,59 \text{ g/l}$ ($0,5 \cdot 10^{-2} \text{ mol/l} \leq [\text{Cu}^+] \leq 2,5 \cdot 10^{-2} \text{ mol/l}$); and $0,69 \text{ g/l} \leq [\text{Ga}^{3+}] \leq 2,79 \text{ g/l}$ ($1 \cdot 10^{-2} \text{ mol/l} \leq [\text{Ga}^{3+}] \leq 4 \cdot 10^{-2} \text{ mol/l}$).

Such a method allows to provide an AuCuGa alloy coating having brightness and ductility properties which are equivalent to those of the prior art AuCuCd alloy coatings.

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Description

BACKGROUND OF THE INVENTION

1. Field of the invention

[0001] The present invention relates to a method of producing gold-copper-gallium alloys (AuCuGa) using an electrolysis process, having the requisite qualities as to ductility, brightness, and which is particularly suitable for applications in jewelry and goldsmith's trade.

2. Description of the related art

[0002] The coating of an alloy based on gold-copper-cadmium (AuCuCd) is well known in the art of jewellery and goldsmith's trade because of its qualities relating to ductility and brightness. For instance, in the most commonly used 18-carat AuCuCd alloy coating, gold is 75% in weight, copper is 18% in weight and cadmium is 7% in weight, which corresponds, respectively, to 52.4%, 39% and 8.6% in atomic percent. This type of alloy coating has the desirable brightness and hardness (about 400 Vickers) and ductility which makes it attractive and thus has been widely used since the last century.

[0003] The co-deposition of gold, copper and cadmium (AuCuCd) using an electrolysis process is well known. Many electrolysis process use different types of electrolytes such as cyanide acid, basic, neutral or sulfuric electrolytes, so as to obtain an AuCuCd alloy coating, insofar as potentials needed with the electrodeposition of the gold, copper and cadmium cations are all in the same range when using the above mentioned electrolytic baths.

[0004] In particular, US patent application No 72/237513 (CH556916 & CH542934) discloses a coating method and an electrolytic bath for depositing a low-carat (14-19 carats) thick AuCuCd coating (20-40 μm), which consists of electrodepositing an AuCuCd alloy from an alkaline aqueous bath containing a soluble gold cyanide complex, a soluble copper cyanide, a soluble cadmium compound, free cyanide and a water-soluble polyoxalcoylenic brightening agent. When depositing a low-carat alloy (i.e. having a low concentration of gold and a high concentration of copper and cadmium), the use of brightness agents allows to obtain a final thick coating which has the desired brightness.

[0005] However, despite the above mentioned advantages of an AuCuCd alloy coating, cadmium is very volatile and toxic. This problem has bad consequences when soldering jewels made of this alloy coating. In particular, when manufacturing an electroformed piece with such an alloy, in which two openings have to be made so as to eliminate the base material therein and then to be filled up by soldering, the volatility and toxicity of cadmium is creating a very serious problem. Furthermore, since 1980, the European regulation tends to limit the use of this compound for health reasons.

[0006] Therefore, there is a real need for providing a new alloy having qualities which are equivalent to those of an AuCuCd alloy, thereby avoiding the above mentioned volatility and toxicity problems of the AuCuCd alloys of the prior art.

[0007] Gold and copper binary alloys of (AuCu) which do not use any cadmium are mentioned in the publication "Galvano-Organo Traitement de Surface", p. 379-382, April 91/615. However, none of such alloys are available on the market. Indeed, it seems that the color of such binary alloy tends to be reddish, and this alloy is very sensitive to oxidation because of the surplus of copper which is needed to compensate for the absence of cadmium. Consequently, such an alloy can hardly be considered suitable for jewellery applications.

[0008] Until now, some compounds have been proposed instead of cadmium for a ternary alloy based on gold, such as zinc (Zn) in AuCuZn alloys (e.g. see US 5,085,744, EP 0 304 315, or EP 0 480 876), Bismuth (Bi) in AuCuBi alloys (e.g. see EP 0 126 921), and silver (Ag) in AuCuAg alloys (see EP 0 566 054), however, none of these alloys have been considered as suitable for jewellery and goldsmith's trade applications. In particular, gallium has never been considered as being a possible alternative for replacing cadmium in gold based alloys due to its melting point (gallium melts at 45°C). This renders the measurements needed to characterize the final alloys very difficult. It is therefore hard to control the behavior of gallium in such AuCuGa ternary alloys.

[0009] A bulk alloy of AuCuGa is used in the field of dentistry, however, this bulk alloy is produced by melting together gold, copper and gallium into ingot, such producing method not being applicable in jewellery applications.

SUMMARY OF THE INVENTION

[0010] In order to overcome the above mentioned problems of the prior art alloy coating, the main object of the present invention is to provide an AuCuGa alloy coating whose brightness and ductility qualities are similar to those of AuCuCd alloy coatings, thus allowing such AuCuGa alloy coating to be used as an alternative to AuCuCd alloy coating, in particular for jewellery applications.

[0011] This object is achieved by providing a method of producing a gold-copper-gallium (AuCuGa) alloy coating by electrodeposition on a substrate, using an aqueous electrolytic bath, characterized in that said aqueous electrolytic bath comprises potassium aurocyanide (KAu(CN)_2), copper cyanide (CuCN), potassium cyanide (KCN) or sodium cyanide (NaCN), and a soluble gallium compound.

[0012] The above mentioned soluble gallium compound may be at least one of, or a mixture of the following gallium salts, gallium sulfate ($\text{Ga}_2(\text{SO}_4)_3$), gallium (III) chloride (GaCl_3), gallium(III)-2,3-naphthalocyanine chloride (2,3-naphthalocyanine gallium(III) monochlo-

ride salt) ($C_{48}H_{24}ClGaN_8$), gallium(III) nitrate nonahydrate ($Ga(NO_3)_3 \cdot 9H_2O$), gallium(III) nitrate hydrate ($Ga(NO_3)_3 \cdot aq$), gallium nitride (GaN), gallium(III) oxide (Ga_2O_3), Gallium phosphide (GaP), and gallium(III) phthalocyanine chloride (Phthalocyanine gallium(III) monochloride salt) ($C_{32}H_{16}ClGaN_8$).

[0013] The molar concentration of gold cations ($[Au^+]$), copper cations ($[Cu^+]$) and gallium cations ($[Ga^{3+}]$) in the electrolytic bath is respectively comprised within the following ranges: $0,19 \text{ g/l} \leq [Au^+] \leq 2,17 \text{ g/l}$ ($0,1 \cdot 10^{-2} \text{ mol/l} \leq [Au^+] \leq 1,1 \cdot 10^{-2} \text{ mol/l}$); $0,31 \text{ g/l} \leq [Cu^+] \leq 1,59 \text{ g/l}$ ($0,5 \cdot 10^{-2} \text{ mol/l} \leq [Cu^+] \leq 2,5 \cdot 10^{-2} \text{ mol/l}$); and $0,69 \text{ g/l} \leq [Ga^{3+}] \leq 2,79 \text{ g/l}$ ($1 \cdot 10^{-2} \text{ mol/l} \leq [Ga^{3+}] \leq 4 \cdot 10^{-2} \text{ mol/l}$).

[0014] In a preferred embodiment, the molar concentration of gold cations ($[Au^+]$), copper cations ($[Cu^+]$) and gallium cations ($[Ga^{3+}]$) in the electrolytic bath is respectively: $[Au^+] = 1,97 \text{ g/l}$ (10^{-2} mol/l), $[Cu^+] = 1,27 \text{ g/l}$ ($2 \cdot 10^{-2} \text{ mol/l}$), and $[Ga^{3+}] = 1,39 \text{ g/l}$ ($2 \cdot 10^{-2} \text{ mol/l}$).

[0015] Further, the mole concentration of potassium cyanide in the electrolytic bath has to be at least about 1,5 the mole concentration of copper cyanide.

[0016] The pH of the electrolytic bath is in the range of 7 to 13, advantageously superior or equal to 10 (more preferably 12), the temperature of the electrolytic bath is in the range of 15 to 80°C , and preferably 50 to 70°C , or about 60°C , and the current density during the electrolysis is in the range of 1.1 to 1.8 A/dm^2 (preferably 1.4 A/dm^2).

[0017] In order to improve the brightness, color and/or chemical properties of the alloys, some complexing agents such as chelating agents or some mixtures thereof, may be added to the aqueous electrolytic bath.

[0018] For instance, said at least one chelating agent is an organophosphate chelating agent or an aminocarboxy or aminopolycarboxy acid, and, in particular, an ethylenediamine tetraacetic acid (EDTA), a nitrilotriacetic acid (NTA), and/or a 2-aminoethanesulfonic acid (taurine).

[0019] The present invention also concerns any AuCuGa alloys produced by such a method.

[0020] Other characteristics and advantages of the present invention will become evident when reading the following detailed description of an embodiment of the present invention, with reference to figure 1 which represents an exemplary galvanostatic assembly suitable for the method of producing an 18-carat AuCuGa alloy coating according to an embodiment of the present invention.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

[0021] As shown in figure 1, an exemplary galvanostatic assembly comprises a tank 3 containing an electrolytic bath in which an anode 1 and a cathode 2 are submerged, a motor 4 for rotationally driving cathode 2, and a current generator 5 connected to both anode 1

and cathode 2. A thermocouple 6 is coupled to an electrical heating device 7 for maintaining a predetermined temperature of the electrolytic bath. A magnetic agitator 8 maintains a stable homogeneity of the electrolytic bath before and during the electrolysis.

[0022] In the described embodiment, cathode 2 is a copper plate covered with a thin gold film which is in the range of 0,1 to $0,2 \mu\text{m}$ thick and which is used as an underlayer. This plate is hung from a copper wire and is rotationally driven by motor 4 at 7,5 rpm. The cathode may be made of any other electrically conductive material such as, for instance, nickel, and may be covered with any other suitable underlayer. Anode 1 is made of a platinum-coated titanium (Ti-Pt), and magnetic agitator 8 is driven at 125 rpm to obtain the desired agitation. The thermocouple maintains the bath temperature at 60°C .

[0023] Beforehand, the substrate of cathode 2 is prepared by skimming off any grease on the substrate so as to dissolve emulsified grease, and by carrying out an activation and a rising process using ultrasounds for removing impurities, followed by rinsing the substrate with distilled water.

[0024] According to the particular embodiment of the present invention, an electrolytic bath with pH = 12 is prepared in the above mentioned tank 3, and cyanide complexes are added thereto in an order described hereafter, so as to obtain an electrolytic bath according to the invention. Potassium aurocyanide $KAu(CN)_2$, copper cyanide ($CuCN$), potassium cyanide (KCN), and gallium sulfate ($Ga_2(SO_4)_3$) are added to the electrolytic solution under the aforementioned agitation, cathode-rotation, temperature and pH conditions, so as to obtain the following molar concentration -for cations: $[Au^+] = 1,97 \text{ g/l}$ (10^{-2} mol/l), $[Cu^+] = 1,27 \text{ g/l}$ ($2 \cdot 10^{-2} \text{ mol/l}$), and $[Ga^{3+}] = 1,39 \text{ g/l}$ ($2 \cdot 10^{-2} \text{ mol/l}$).

[0025] In this particular embodiment, gallium (III) sulfate anhydrous ($Ga_2(SO_4)_3$) is used so as to provide the electrolytic bath with gallium cations. However many other type of gallium salts, or mixtures of these salts, may be used, as, for instance, gallium(III) chloride ($GaCl_3$), gallium(III)-2,3-naphthalocyanine chloride (2,3-naphthalocyanine gallium(III) monochloride salt) ($C_{48}H_{24}ClGaN_8$), gallium(III) nitrate nonahydrate ($Ga(NO_3)_3 \cdot 9H_2O$), gallium (III) nitrate hydrate ($Ga(NO_3)_3 \cdot aq$), gallium nitride (GaN), gallium(III) oxide (Ga_2O_3), Gallium phosphide (GaP), or gallium(III) phthalocyanine chloride (Phthalocyanine gallium(III) monochloride salt) ($C_{32}H_{16}ClGaN_8$).

[0026] The addition of potassium cyanide or sodium cyanide in the electrolytic solution is required so as to make the copper cyanide soluble. The mole concentration of potassium cyanide has to be at least about 1,5 the one of copper cyanide, i.e. in the present particular embodiment, $[K^+] = 1,173 \text{ g/l}$ ($3 \cdot 10^{-2} \text{ mol/l}$). However, any other cyanide complex enhancing the solubility of copper cyanide may be used in the electrolytic bath.

[0027] Then, while still maintaining the same experi-

mental conditions, a current density of 1.4 A/dm² is applied between anode 1 and cathode 2 for activating the electrolysis of the solution.

[0028] The agitation of the bath and the rotation of the cathode facilitate the diffusion of the cations by opposing the exhaustion of the diffusion layer. The stronger the agitation, the more the current density required for maintaining the electrolysis is high, and accordingly the quickest the coating is achieved. However, in the present case of the AuCuGa alloy coating, the agitation and rotation conditions advantageously further assist in eliminating any hydrogen bubbles which may occur at the surface of the cathode when the water reduces, such hydrogen bubbles normally disturbing the co-deposition of the three metal cations and thus impairing the properties of the final alloy coating. Since the gallium reduction occurs beyond the water reduction (the reduction potential of H₂O is about -2 V), it is necessary to provide a operating potential greater than -2 V so as to reduce the three metals. In this particular embodiment of the present invention, the operating potential is about -2.75 V.

[0029] The above-mentioned deposition conditions are maintained for a certain period of time depending on the desired thickness of the coating. In the present embodiment, a thickness of 4 µm is obtained after a 10 minutes lasting application of the mentioned current density. A larger thickness may be obtained by increasing the time period of applying the potential between the anode and the cathode.

[0030] After stopping the electrolysis, and when the coating is 4 µm thick, plate 2 is removed from the electrolytic bath to be washed, depending on the future use of the plate.

[0031] In this particular embodiment, the final alloy coating is a 18-carat ternary AuCuGa alloy with a chemical composition, in atomic percent, of 62% of Au, 27.3% of Cu and 10.7% of Ga.

[0032] This alloy has a hardness which is suitable for applications to jewellery and goldsmith's trade. The measured average grain size is about 0.3 µm, which results in a brightness of the AuCuGa alloy coating similar to that of prior art AuCuCd alloy coatings. Furthermore, as the surface is no more rough, this also constitutes an advantage due to an increased resistance to corrosion. The color of the AuCuGa alloy coating according to the invention is slightly less golden than the prior art AuCuCd alloy.

[0033] Further, the aging tests which have been conducted on the AuCuGa alloy coating according to the invention, have shown that it is not sensitive to corrosion and tarnishment caused by air, sweat and/or acetic acid.

[0034] The present invention is not limited to the above exemplary described preferred embodiment. In particular, many different types of AuCuGa alloys having different carat contents (e.g. from 8 to about 24 carats) and similar properties in terms of brightness, may be obtained by using the method according to the invention.

The molar concentration of the different cations in the electrolytic bath may be comprised within the following ranges : 0,19 g/l ≤ [Au⁺] ≤ 2,17 g/l (0,1.10⁻² mol/l ≤ [Au⁺] ≤ 1,1.10⁻² mol/l) ; 0,31 g/l ≤ [Cu⁺] ≤ 1,59 g/l (0,5.10⁻² mol/l ≤ [Cu⁺] ≤ 2,5.10⁻² mol/l) ; and 0,69 g/l ≤ [Ga³⁺] ≤ 2,79 g/l (1.10⁻² mol/l ≤ [Ga³⁺] ≤ 4.10⁻² mol/l).

[0035] According to the present invention, the electrolysis may be carried out in an aqueous electrolytic bath having a pH value equal to or greater than 10. The pH value of the electrolytic bath may be varied to influence the yield of the electrolysis (mg/A.min.) as well as the hardness of the coating.

[0036] The temperature of the electrolytic bath may be comprised in the range of 50 to 70°C. By increasing of the temperature, it is possible to increase the admissible maximum current density, the viscosity will then decrease, and accordingly the electrochemical reaction and diffusion speed increase. Therefore, the electrolytic deposition may be made with electrolytes of a higher concentration.

[0037] The operating current density may be in the range of 1.1 to 1.8 A/dm².

[0038] The deposition conditions which allow to provide the AuCuGa alloy coating according to the invention with the above mentioned properties, have been checked by analyzing the final alloy with different well-known chemical and structural characterization techniques such as the Electron Spectroscopy for Chemical Analysis (ESCA), the Energy Dispersive X-Ray Spectroscopy (EDXS), the atomic absorption spectroscopy or the X-ray diffraction and by using Scanning Electron Microscopy (SEM).

[0039] The experimental implementation of different depositions under variable potentials controlled by ESCA has allowed to determine the correct ranges of the parameters. The ESCA analysis has shown the order in the reduction of the cations (for potentials more and more negative: gold, copper, then gallium) and the EDXS has allowed to determine the chemical composition of the final alloys having a thickness of 1 to 4 µm. The EDXS analysis has allowed to determine the surface composition of the alloys. For thicker alloys, i.e. greater than 4 µm, the chemical composition of the whole deposition was analyzed by atomic absorption spectroscopy. The analysis of the X-ray diffraction diagram established the existence of a periodical structure in the electro-deposit according to the invention.

[0040] Further, in the AuCuGa alloy, the copper content may be controlled by either increasing the copper concentration of the electrolytic bath (resulting in significant changes), or by increasing the current density (resulting in slight changes). On the other hand, it was established that the gallium content of the alloy does not change in a simple manner when increasing the current density. Thus, the increase of the current facilitates the co-deposition of gallium and copper. Therefore, another advantage of the present invention is that the change in gold content (number of carats or the content of copper

and gallium) may be controlled by adjusting the current density between both electrodes.

[0041] Some additives (brightness agents for refining the grains, leveling agents such as soluble selenium or tellurium compounds, colloids, wetting agents, ...) may be added to the electrolytic bath according to the invention, so as to improve the yield or to modify the co-deposition structure and improve the brightness and/or color of the AuCuGa coating. For instance, some polyoxalcoylenic compounds may be used as brightness agents and some chelating agents like organophosphate chelating agents or aminocarboxy acids (or aminopolycarboxy acids) may be used.

[0042] For instance, the addition of ethylenediamine tetraacetic acid (EDTA, abbrev. H_2Y) or nitrilotriacetic acid (NTA, abbrev. H_3X) (e.g. molar concentrations in the range of 0,1 to 2 mol/l) to the electrolytic bath may improve the brightness and give a rosy color to the coating. Experiments have shown that under a current density of 1,4 A/dm² during the electrolysis, the increasing of EDTA or NTA lowers the reduction of gold and gallium and increases the reduction of copper. The increasing in current density slightly increases the reduction of copper.

[0043] In particular, It has been experimented that the addition of taurine (2-amino ethanesulfonic acid, $NH_2CH_2CH_2SO_3H$) to the electrolytic bath makes it possible to get AuCuGa ternary alloys under current densities of about 1 A/dm², and to increase the cathodic efficiency of the method. The increasing of taurine lowers the reduction of gold and increases the reduction of gallium and copper. The increasing in current density slightly increases the reduction of copper.

[0044] The alloy according to the invention is particularly suitable for 15-carats to 24-carats coating applications for jewelry or goldsmith's trade, and is also suitable for any other application which requires the use of such an alloy, as for instance, in the microelectronic techniques.

Claims

1. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition on a substrate (2), using an aqueous electrolytic bath, characterized in that said aqueous electrolytic bath comprises potassium aurocyanide ($KAu(CN)_2$), copper cyanide ($CuCN$), potassium cyanide KCN or sodium cyanide ($NaCN$), and a soluble gallium compound.
2. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition on a substrate, according to claim 1, wherein the soluble gallium compound is at least one, or a mixture of, gallium sulfate ($Ga_2(SO_4)_3$), gallium(III) chloride ($GaCl_3$), gallium(III)-2,3-naphthalocyanine chloride

(2,3-naphthalocyanine gallium(III) monochloride salt) ($C_{48}H_{24}ClGaN_8$), gallium(III) nitrate nonahydrate ($Ga(NO_3)_3 \cdot 9H_2O$), gallium(III) nitrate hydrate ($Ga(NO_3)_3 \cdot aq$), gallium nitride (GaN), gallium(III) oxide (Ga_2O_3), Gallium phosphide (GaP), and gallium(III) phthalocyanine chloride (Phthalocyanine gallium(III) monochloride salt) ($C_{32}H_{16}ClGaN_8$).

3. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to claim 1 or 2, wherein the molar concentration of gold cations ($[Au^+]$), copper cations ($[Cu^+]$) and gallium cations ($[Ga^{3+}]$) in the electrolytic bath is respectively comprised within the following ranges : 0,19 g/l $\leq [Au^+] \leq 2,17$ g/l ($0,1 \cdot 10^{-2}$ mol/l $\leq [Au^+] \leq 1,1 \cdot 10^{-2}$ mol/l) ; 0,31 g/l $\leq [Cu^+] \leq 1,59$ g/l ($0,5 \cdot 10^{-2}$ mol/l $\leq [Cu^+] \leq 2,5 \cdot 10^{-2}$ mol/l) ; and 0,69 g/l $\leq [Ga^{3+}] \leq 2,79$ g/l ($1 \cdot 10^{-2}$ mol/l $\leq [Ga^{3+}] \leq 4 \cdot 10^{-2}$ mol/l).
4. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to any one of the preceding claims, wherein the molar concentration of gold cations ($[Au^+]$), copper cations ($[Cu^+]$) and gallium cations ($[Ga^{3+}]$) in the electrolytic bath is respectively : $[Au^+] = 1,97$ g/l (10^{-2} mol/l), $[Cu^+] = 1,27$ g/l ($2 \cdot 10^{-2}$ mol/l), and $[Ga^{3+}] = 1,39$ g/l ($2 \cdot 10^{-2}$ mol/l).
5. Method of producing a gold-copper-gallium (AuCu-Ga) alloy by electrodeposition according to any one of the preceding claims, wherein the mole concentration of potassium cyanide has to be at least about 1,5 the mole concentration of copper cyanide.
6. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to any one of the preceding claims, wherein the pH-value of the electrolytic bath is in the range of 7 to 13.
7. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to claim 6, wherein the pH-value of the electrolytic bath is equal to or greater than 10.
8. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to any one of the preceding claims, wherein the temperature of the electrolytic bath is in the range of 15 to 80°C.
9. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to claim 8, wherein the temperature of the electrolytic bath is in the range of 50 to 70°C.
10. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to

claim 9, wherein the temperature of the electrolytic bath is about 60°C.

11. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to any one of the preceding claims, wherein the current density during the electrolysis is in the range of 1.1 to 1.8 A/dm². 5
12. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to any one of the preceding claims, wherein said aqueous electrolytic bath comprises at least one chelating agent. 10
13. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to claim 12, wherein said at least one chelating agent is an organophosphate chelating agent or an aminocarboxy or aminopolycarboxy acid. 15 20
14. Method of producing a gold-copper-gallium (AuCu-Ga) alloy coating by electrodeposition according to claim 13, wherein said one chelating agent is an ethylenediamine tetraacetic acid (EDTA), a nitrilotriacetic acid (NTA) , and/or a 2-aminoethanesulfonic acid (taurine). 25
15. A gold-copper-gallium alloy coating produced by a method according to any one of the preceding claims. 30

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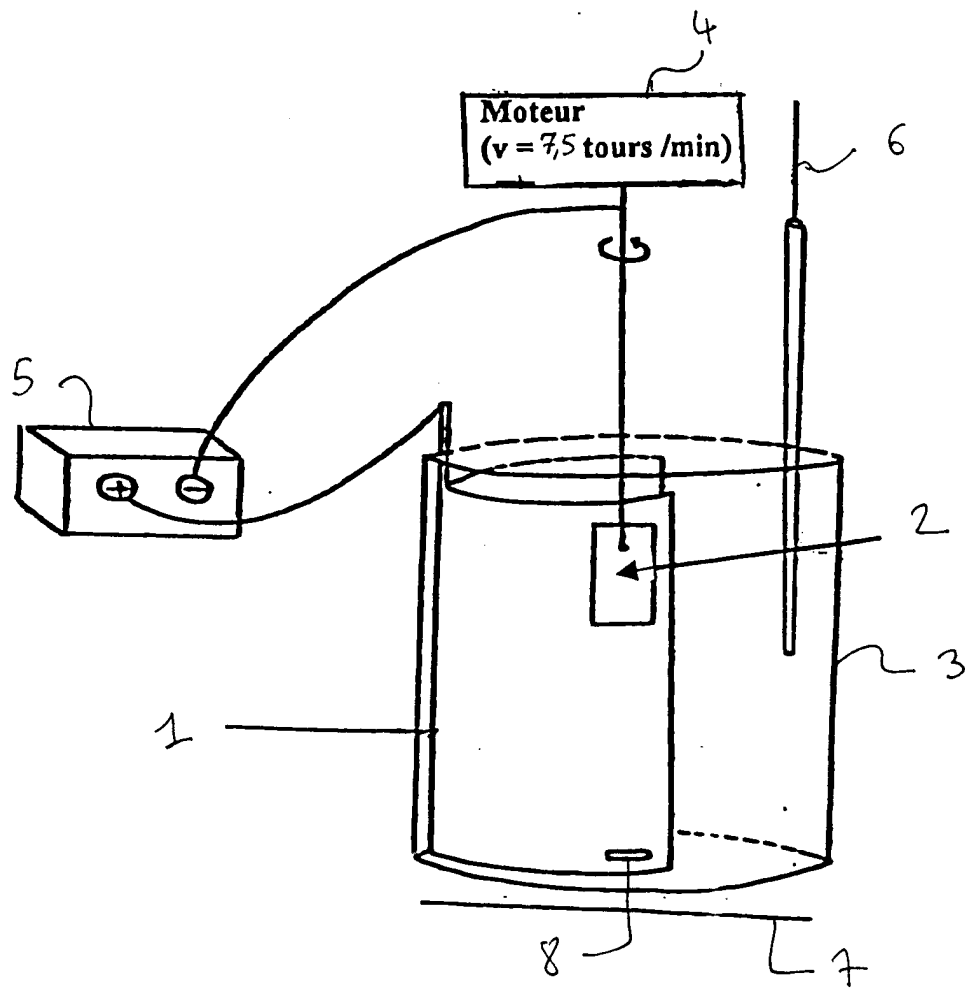


Fig 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 40 2969

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	FR 2 405 312 A (OXY METAL INDUSTRIES CORP) 4 May 1979 (1979-05-04)		C25D3/62
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 May 2000	Examiner Van Leeuwen, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 99 40 2969

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82