

(19)



(11)

EP 2 669 407 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

30.03.2022 Bulletin 2022/13

(51) International Patent Classification (IPC):

C25D 3/62 ^(2006.01) **C25D 7/00** ^(2006.01)

(52) Cooperative Patent Classification (CPC):

C25D 3/62; C25D 7/005

(21) Application number: **13170067.6**

(22) Date of filing: **31.05.2013**

(54) **Galvanic baths for obtaining a low-carat gold alloy, and galvanic process that uses said baths**

Galvanische Bäder zur Herstellung einer niederkarätigen Goldlegierung und galvanischer Process verwendet diese Bäder

Bains galvaniques pour obtenir un alliage d'or de bas carat, et procédé galvanique qui utilise ces bains

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

• **Innocenti, Massimo**

59016 Poggio a Caiano (IT)

• **Bencista, Ilaria**

50100 Firenze (IT)

(30) Priority: **01.06.2012 IT FI20120103**

(74) Representative: **Valenza, Silvia et al**

Notarbartolo & Gervasi S.p.A.

Viale Achille Papa, 30

20149 Milano (IT)

(43) Date of publication of application:

04.12.2013 Bulletin 2013/49

(73) Proprietor: **BLUCLAD S.p.A.**

59100 Prato (IT)

(56) References cited:

EP-A1- 2 135 972 EP-A2- 0 188 386

WO-A1-2009/037180 GB-A- 2 028 873

JP-A- 2000 319 794 US-A- 3 174 918

US-A- 3 878 066 US-A- 3 883 409

US-A- 4 088 549 US-A- 6 165 342

US-A1- 2006 283 714

(72) Inventors:

• **Cavaciocchi, Lorenzo**

50058 Signa (IT)

• **Banchelli, Elena**

59100 Prato (IT)

• **Canelli, Danilo Vincenzo**

51037 Montale (IT)

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 669 407 B1

Description

Field of the invention

[0001] The invention relates to the field of compounds used in galvanic processes, in particular galvanic baths for obtaining a low-carat gold alloy, and to the galvanic process for obtaining said alloy.

Prior art

[0002] Galvanic baths containing considerable amounts of toxic substances, such as cyanides, and heavy metals, which are also toxic and difficult to remove, for example cadmium, in the matrix (where matrix means an aqueous solution of organic and inorganic acids and salts thereof) have been used for decades to obtain a gold alloy containing less than 75% by weight of gold as metal (corresponding to a gold alloy of 18 carats or less).

[0003] These baths make it possible to effectively obtain gold deposits having the desired carat value and considerable thicknesses, however the presence therein of highly poisonous substances makes them virtually unacceptable for practical use.

[0004] In order to overcome the aforementioned disadvantages, alternatives to the formulations have been sought that in particular would substitute cyanide, as a complexing agent, and cadmium, as a binder, in combination with copper.

[0005] Previous alternatives in use, however, utilise products that have only partly solved the known problems encountered with the use of the prior galvanic baths and, in addition, do not demonstrate the same suitability for practical use and the same quality of the results: in fact, these are generally formulations which only partly eliminate the toxic products used and which have restricted periods of use or with which an alloy is obtained having characteristics of carat value, thickness or appearance that fail to meet the needs of the intended purpose: in particular, nonuniform deposits or deposits having colourations that are too inclined towards pink and red for the aesthetic purposes for which they are used are obtained.

[0006] However, baths of this type also include baths that utilise cyanide in the matrix or that, although they do not contain cyanide in the matrix, contain other doped elements of a certain toxicity.

[0007] For example, US4358351 describes a bath containing gold, copper, zinc, free cyanide and arsenic as gloss additive; US4487664 describes a bath containing gold-silver and free cyanide; US5085744 describes a bath containing gold, copper, zinc, free cyanide and antimony as gloss additive; US4687557 describes a bath containing gold, copper, and cadmium devoid of free cyanide in solution. WO 2009/037180 describes a gold alloy plating bath comprising gold, copper and indium ions and free cyanide.

[0008] It is therefore obvious in the light of the foregoing

that it would be greatly desirable, from the industrial point of view, to make available galvanic baths that are practically free from the above-mentioned toxic substances, are practical in use and make it possible to obtain a precise carat value in the 12 - 18-carat range, suitable thicknesses, uniform deposit and colour tending towards the yellow typical of a gold deposit.

Detailed description of the invention

[0009] The present invention makes it possible to satisfy the above-mentioned needs due to alkaline galvanic baths according to claim 1.

[0010] In accordance with the present invention, "galvanic bath" means the aqueous solutions in which the surfaces to be treated by means of the galvanic process are immersed.

[0011] In accordance with the present invention, the gold salts are preferably selected from: potassium dicyanoaurate, potassium tetracyanoaurate, ammonium cyanoaurate, or a combination thereof.

[0012] It is noted that, by contrast with the above-cited prior art, cyanide is not present in the matrix of the bath in the present invention and its content in the galvanic solution is caused by its counterion function in the gold salts alone and is therefore practically irrelevant, although necessary, for the stability of the gold in solution.

[0013] The amount of gold, calculated on the basis of the respective salts, is between 0.7 and 4 g/L, preferably between 1.5 and 3 g/L, in order to achieve the desired efficiency and thicknesses.

[0014] In accordance with the invention, copper salts means, for example: sulfate, phosphate, pyrophosphate, chloride, or other salts that are stable under the working conditions of the bath.

[0015] Copper, calculated on the basis of the respective salts, is present in an amount between 0.3 and 2.5 g/L, preferably between 0.5 and 2 g/L, in relation to the desired carat value in the 12 - 18 carat range.

[0016] Indium salts useful in accordance with the invention are, for example: chloride, sulfate, citrate, tartrate, gluconate, or any other organic or amine complex compatible with the working conditions of the bath.

[0017] The concentration of indium, calculated on the basis of the respective salts, ranges from 0.1 to 2 g/L, preferably from 0.5 to 1.5 g/L, in relation to the desired carat value in the 12 - 18 carat range.

[0018] The matrix of the bath is formed by polycarboxylic acid salts having both buffer characteristics and complexing power, such as citrates, tartrates, gluconates, maleates, malonates, possibly in combination with the corresponding acids for creation of the expedient buffer, and possibly mixed together in order to achieve the expedient complexing power.

[0019] These acids and the respective salts are each used in an amount ranging from 30 to 150 g/L, more commonly from 50 to 100 g/L.

[0020] Complexing agents that can be expediently

used in order to improve the stability of the metals in solution and to regulate the properties thereof in alloy include, for example, ethylenediaminetetraacetic acid and salts thereof, etidronic acid and salts thereof, ethylenediamine tetramethyl phosphonic acid and salts thereof, iminodiacetic acid and salts thereof, nitrilotriphosphonic acid and salts thereof, and nitrilotriacetic acid and salts thereof; these complexing agents normally being used in amounts ranging from 1 to 50 g/L according to the complexing power of each one thereof, a person skilled in the art knowing which complexing agent will be the most suitable for use and in what amounts and combinations, according to the desired carat value in the 12 - 18 carat range.

[0021] A complexing and regulatory action of the alloy metals is due to the amine component of the bath.

[0022] In particular, it has been found that some types of amine enable finer regulation of the percentage of indium in alloy.

[0023] In particular, the amines used for this purpose are triethylenetetramine, diethylenetetramine, ethylenediamine and tetraethylenepentamine.

[0024] The amine in question is used in amounts ranging from 0.05 to 1 g/L, more expediently from 0.1 to 0.7 g/L, depending on the desired percentage of indium in alloy, within the carat range from 12 to 18 carats.

[0025] The bath may also obviously contain other components normally used in galvanic processes for their glossing and surfactant action.

[0026] In particular due to the glossing action, it is expedient to add elements, such as silver, tellurium, bismuth, iron, zinc, iridium, rhenium, vanadium, molybdenum, tungsten, in such a form so as to be soluble and stable under the working conditions; the amounts to be used range from 0.005 to 0.2 g/L of element as such, and more in particular from 0.010 to 0.1 g/L.

[0027] The formulations according to the invention may also comprise sulfated compounds, such as organic thiols belonging to the classes of mercaptotetrazoles, mercaptopyrimidines, mercaptopyrrols, mercaptoimidazoles and mercaptotriazoles, possibly containing a sulfur atom in the aromatic ring, possibly having a nitrogen ring condensed with a benzene ring, having one or more thio groups.

[0028] It has been observed that the general effect of these substances is that of regulating the deposition of the gold, improving the uniformity of the deposit and reducing the tendency thereof towards chemical deposition and stain formation.

[0029] The amounts to be used expediently range from 0.01 to 0.500 g/L, and more in particular from 0.05 to 0.200 g/L.

[0030] The surfactants have both glossing and surfactant action, and those used normally within galvanic scope in baths having matrices of this type are used in this invention: a person skilled in the art will be able to identify the most suitable type to use; however, the amounts used are never greater than 0.005 L/L of an

aqueous solution thereof (10% w/v): higher doses lower the efficiency of the bath and create interference with the regular properties of the metals in alloy.

[0031] The bath preferably functions in a pH range between 7 and 12, and more expediently between 8 and 10; the pH is regulated with organic acids belonging to the selected buffer pair, or with mineral acids such as sulfuric acid, phosphoric acid, sulfamic acid, methanesulfonic acid, pyridinesulfonic acid, or with alkali metal hydroxides, such as potassium and sodium.

[0032] The pH is not a critical parameter in this formulation for obtaining a precise carat value, but it is fundamental that the pH is alkaline for the stability of the components in solution.

[0033] The working temperature of the galvanic bath in question is preferably between 50°C and 70°C; however, this is not a critical parameter for obtaining a precise carat value.

[0034] The current to be applied to the galvanic bath according to the invention is normally between 0.5 - 3 A/cm², preferably 0.7 - 2 A/cm².

[0035] The application times vary according to the amperage imposed and the desired thickness: with the bath according to the invention, it is possible to obtain deposits having thicknesses up to 500 microns.

[0036] By expediently varying the applied current, it is possible to obtain alloys of different carat value and colour, since increasing the current applied causes a reduction of the gold in alloy and increases the copper, thus resulting in lower carat values and colours tending more greatly towards red, whereas, vice versa, reducing the current applied causes an increase of the gold in alloy and therefore higher carat values and colours tending more greatly towards yellow.

[0037] It is therefore possible to achieve any intermediate percentage in the 12 - 18-carat value range in a precise manner by imposing the expedient current.

[0038] Using the baths as described above, gold alloys in which the gold varies from 50% to 75% (percentages expressed in weight) are obtained by deposit at the cathode of the galvanic cell.

Example 1

[0039] A bath having the following composition was prepared:

Citric acid: 50 g/L

Potassium citrate: 120 g/L

Tetrasodium EDTA: 30 g/L

Gold: 1.2 g/L as metal, introduced as potassium dicyanoaurate

Copper: 0.7 g/L as metal, introduced as copper sulfate

Indium: 0.3 g/L as metal, introduced as indium sulfate

Ethylenediamine 0.2 mL/L as pure substance, introduced as aqueous solution 50% w/v

Silver 0.05 g/L as metal, introduced as silver cyanide salt 80.6%

The bath was brought to pH 8.5 with potassium hydroxide and heated to 60°C.

[0040] A current of 0.7 A/cm² was applied for 3 minutes to a sheet of nickel-plated brass having a surface area of 0.5 cm², suitably de-greased and re-rinsed with deionised water.

[0041] At the end of the period, the sheet was rinsed with deionised water and dried by compressed air.

[0042] The colour coordinates measured in accordance with CIELab parameters were as follows: L= 79.2 a= 1.8 b= 13.6

[0043] Corresponding to an alloy definable as 14 carats.

Example 2

[0044] A bath having the following composition was prepared:

Sodium gluconate: 60 g/L

Iminodiacetic acid: 80 g/L

Gold: 2.5 g/L as metal, introduced as potassium dicyanoaurate

Copper: 1.8 g/L as metal, introduced as copper sulfate

Indium: 0.35 g/L as metal, introduced as indium sulfate

Diethylenetetramine 0.1 mL/L as a pure substance, introduced as aqueous solution 50% w/v

Rhenium 0.05 g/L as metal, introduced as sodium perrhenate 2-(2-pyrazine)ethane thiol 0.01 g/L as pure substance, introduced in the bath as aqueous solution 10% w/v

[0045] The bath was brought to pH 9.5 with potassium hydroxide and heated to 60°C.

[0046] A current of 1.5 A/cm² was applied for 5 minutes to a sheet of nickel-plated brass having a surface area of 0.5 cm², suitably de-greased and re-rinsed with deionised water.

[0047] At the end of the period, the sheet was rinsed with deionised water and dried by compressed air.

[0048] The colour coordinates measured in accordance with CIELab parameters were as follows: L= 84.8 a= 5.1 b= 16.2

[0049] The surface of the alloy was analysed by electronic scan microscope; the following percentages were found

Au: 74% In: 5% Cu: 22%

Corresponding to an alloy definable as 18 carats.

Claims

1. A galvanic bath comprising aqueous solutions having an alkaline pH and comprising gold salts, copper salts and indium salts, organic polycarboxylic acid salts, organic amines, and possibly complexing agents, sulfurated compounds, surfactants and other metals, wherein the concentration of indium, calculated on the basis of the respective salts, ranges from 0.1 to 2 g/L; wherein said organic amines are selected in the group consisting of triethylenetetramine, diethylenetetramine, ethylenediamine and tetraethylenepentamine; said amines used in amounts ranging from 0.05 to 1 g/L; said complexing agent are selected in the group consisting of ethylenediaminetetraacetic acid and salts thereof, etidronic acid and salts thereof, ethylenediamine tetramethyl phosphonic acid and salts thereof, iminodiacetic acid and salts thereof, nitrilotriphosphonic acid and salts thereof, and nitrilotriacetic acid and salts thereof; said sulfurated compounds are selected in the group consisting of organic thiols belonging to the classes of 2-(2-pyrazine)ethane thiol, mercaptotetrazoles, mercaptopyrimidines, mercaptopyrroles, mercaptoimidazoles and mercaptotriazoles, possibly containing a sulfur atom in the aromatic ring, possibly having a nitrogen ring condensed with a benzene ring, having one or more thio groups; said surfactants having both glossing and surfactant action and being those normally used within galvanic baths having matrices formed by said organic polycarboxylic acid salts; said surfactants used in an amount never greater than 0.005 L/L of a 10% w/v aqueous solution thereof; said other metals having glossing action are selected in the group consisting of silver, tellurium, bismuth, iron, zinc, iridium, rhenium, vanadium, molybdenum, tungsten in such a form so as to be soluble and stable under the working conditions in amounts between 0.005 and 0.2 g/L of element as such; said polycarboxylic acid salts having both buffer characteristics and complexing power, possibly in combination with the corresponding acids for creation of the expedient buffer, these acids and the respective salts are each used in an amount ranging from 30 to 150 g/L; **characterized in that** cyanide is not present in the matrix of the bath and its content in the galvanic solution is caused by its counterion function in the gold salts alone.
2. The galvanic bath according to claim 1, wherein said gold salts are selected from: potassium dicyanoaurate, potassium tetracyanoaurate, ammonium cyanoaurate, or a combination thereof; said copper salts are selected from: sulfate, phosphate, pyrophosphate, chloride, or other salts that are stable under the working conditions of the bath itself, and said indium salts are selected from chloride, sulfate, citrate, tartrate, gluconate, or an organic or amine

complex.

3. The galvanic bath according to claim 2, wherein the amount of gold ranges from 0.7 to 4 g/L, preferably from 1.5 to 3 g/L, the amount of copper is between 0.3 and 2.5 g/L, preferably between 0.5 and 2 g/L. 5
4. The galvanic bath according to any one of claims 1-3, wherein said polycarboxylic acid salts are selected from: citrates, tartrates, maleates, malonates, possibly in combination with the corresponding acids for creation of the suitable buffer, and possibly in a mixture of mixtures thereof, and preferably in amounts between 50 and 100 g/L. 10
5. The galvanic bath according to any one of claims 1-4, wherein said amines are triethylenetetramine and diethylenetetramine, preferably in amounts that vary from 0.1 to 0.7 g/L. 15
6. The galvanic bath according to any one of claims 1-5, wherein said other metals are used in amounts between 0.010 and 0.1 g/L. 20
7. Galvanic baths according to claims 1-6, wherein said sulfurated compounds are present in amounts between 0.01 and 0.500 g/L, and more in particular in amounts between 0.05 and 0.200 g/L. 25
8. Galvanic process for the plating of objects with gold alloys from 12 - 18 carats, wherein the baths according to claims 1 to 7 are used. 30
9. Galvanic process according to claim 8, wherein said process is carried out in a pH range between 7 and 12, at a temperature between 50°C and 70°C, and with a current applied between 0.5 - 3 A/cm². 35

Patentansprüche 40

1. Galvanisches Bad, umfassend wässrige Lösungen mit einem alkalischen pH-Wert, die Goldsalze, Kupfersalze und Indiumsalze, organische Polycarbonsäuresalze, organische Amine und möglicherweise Komplexbildner, schwefelhaltige Verbindungen, Tenside und andere Metalle umfassen, wobei die Konzentration an Indium, berechnet auf der Basis der jeweiligen Salze, im Bereich von 0,1 bis 2 g/l liegt; 45

wobei die organischen Amine ausgewählt sind aus der Gruppe umfassend Triethylentetramin, Diethylentetramin, Ethylendiamin und Tetraethylpentamin; wobei die Amine in Mengen von 0,05 bis 1 g/l verwendet werden; 50
 der Komplexbildner ausgewählt ist aus der Gruppe bestehend aus Ethylendiamintetraessigsäure und deren Salzen, Etidronsäure und

deren Salzen, Ethylendiamintetramethylphosphonsäure und deren Salzen, Iminodiessigsäure und deren Salzen, Nitrilotriphosphonsäure und deren Salzen sowie Nitrilotriessigsäure und deren Salzen;

die sulfurierten Verbindungen ausgewählt sind aus der Gruppe bestehend aus organischen Thiolen, die zu den Klassen 2-(2-Pyrazin)ethanthiol, Mercaptotetrazole, Mercaptopyrimidine, Mercaptopyrrole, Mercaptoimidazole und Mercaptotriazole gehören, die möglicherweise ein Schwefelatom im aromatischen Ring enthalten, möglicherweise einen mit einem Benzolring kondensierten Stickstoffring aufweisen, eine oder mehrere Thiogruppen aufweisen;

wobei die Tenside sowohl eine glänzende als auch eine oberflächenaktive Wirkung haben und solche sind, die normalerweise in galvanischen Bädern mit Matrizen verwendet werden, die durch die organischen Polycarbonsäuresalze gebildet werden; wobei die Tenside in einer Menge verwendet werden, die niemals größer als 0,005 l/l einer 10 Gew.-%-igen wässrigen Lösung davon ist;

die anderen Metalle mit glänzender Wirkung ausgewählt sind aus der Gruppe bestehend aus Silber, Tellur, Wismut, Eisen, Zink, Iridium, Rhenium, Vanadium, Molybdän, Wolfram in einer solchen Form, dass sie unter den Arbeitsbedingungen in Mengen zwischen 0,005 und 0,2 g/l des Elements als solches löslich und stabil sind; diese Polycarbonsäuresalze sowohl Puffereigenschaften als auch komplexbildende Wirkung aufweisen, gegebenenfalls in Kombination mit den entsprechenden Säuren zur Herstellung des zweckmäßigen Puffers, wobei diese Säuren und die jeweiligen Salze jeweils in einer Menge von 30 bis 150 g/l verwendet werden;

dadurch gekennzeichnet, dass Cyanid in der Matrix des Bades nicht vorhanden ist und sein Gehalt in der galvanischen Lösung allein durch seine Gegenionenfunktion in den Goldsalzen bedingt ist.

2. Galvanisches Bad nach Anspruch 1, wobei die Goldsalze ausgewählt sind aus: Kaliumdicyanoaurat, Kaliumtetracyanoaurat, Ammoniumcyanoaurat oder einer Kombination davon; die Kupfersalze ausgewählt sind aus: Sulfat, Phosphat, Pyrophosphat, Chlorid oder anderen Salzen, die unter den Arbeitsbedingungen des Bades selbst stabil sind, und die Indiumsalze ausgewählt sind aus Chlorid, Sulfat, Citrat, Tartrat, Gluconat oder einem organischen oder Aminkomplex. 50
3. Galvanisches Bad nach Anspruch 2, wobei die Menge an Gold im Bereich von 0,7 bis 4 g/l, vorzugsweise von 1,5 bis 3 g/l, liegt und die Menge an Kupfer zwi-

schen 0,3 und 2,5 g/l, vorzugsweise zwischen 0,5 und 2 g/l beträgt.

4. Galvanisches Bad nach einem der Ansprüche 1 bis 3, wobei die Polycarbonsäuresalze ausgewählt sind aus: Citraten, Tartraten, Maleaten, Malonaten, möglicherweise in Kombination mit den entsprechenden Säuren zur Herstellung des geeigneten Puffers und möglicherweise in einer Mischung von Mischungen davon, und vorzugsweise in Mengen zwischen 50 und 100 g/l. 5 10
5. Galvanisches Bad nach einem der Ansprüche 1 bis 4, wobei die Amine Triethylentetramin und Diethylentetramin sind, vorzugsweise in Mengen, die von 0,1 bis 0,7 g/l variieren. 15
6. Galvanisches Bad nach einem der Ansprüche 1-5, wobei die anderen Metalle in Mengen zwischen 0,010 und 0,1 g/l verwendet werden. 20
7. Galvanische Bäder nach einem der Ansprüche 1 bis 6, wobei die schwefelhaltigen Verbindungen in Mengen zwischen 0,01 und 0,500 g/l und insbesondere in Mengen zwischen 0,05 und 0,200 g/l vorhanden sind. 25
8. Galvanisches Verfahren zur Beschichtung von Gegenständen mit Goldlegierungen von 12 - 18 Karat, **dadurch gekennzeichnet, dass** die Bäder nach den Ansprüchen 1 bis 7 verwendet werden. 30
9. Galvanisches Verfahren nach Anspruch 8, wobei das Verfahren in einem pH-Bereich zwischen 7 und 12, bei einer Temperatur zwischen 50 °C und 70 °C und mit einem angelegten Strom zwischen 0,5 - 3 A/cm² durchgeführt wird. 35

Revendications 40

1. Bain galvanique comprenant des solutions aqueuses ayant un pH alcalin et comprenant des sels d'or, des sels de cuivre et des sels d'indium, des sels d'acide polycarboxylique organiques, des amines organiques, et éventuellement des agents de complexation, des composés sulfurés, des tensioactifs et d'autres métaux, dans lequel la concentration en indium, calculée sur la base des sels respectifs, va de 0,1 à 2 g/L ; 45 50

dans lequel lesdites amines organiques sont sélectionnées parmi le groupe constitué de la triéthylènetétramine, de la diéthylènetétramine, de l'éthylènediamine et de la tétraéthylènepentamine ; lesdites amines étant utilisées dans des quantités allant de 0,05 à 1 g/L ; 55

lesdits agents de complexation sont sélectionnés parmi le groupe constitué de l'acide éthylènediaminetétraacétique et de ses sels, de l'acide étidronique et de ses sels, de l'acide éthylènediaminetétraméthylphosphonique et de ses sels, de l'acide iminodiacétique et de ses sels, de l'acide nitrilotriphosphonique et de ses sels, et de l'acide nitrilotriacétique et de ses sels ;

lesdits composés sulfurés sont sélectionnés parmi le groupe constitué des thiols organiques appartenant aux classes du 2-(2-pyrazine)éthanthiol, des mercaptotétrazoles, des mercaptopyrimidines, des mercaptopyrrols, des mercaptoimidazoles et des mercaptotriazoles, contenant éventuellement un atome de soufre dans le cycle aromatique, ayant éventuellement un cycle azoté condensé avec un cycle benzénique, ayant un ou plusieurs groupes thio ;

lesdits tensioactifs ayant à la fois une action lustrante et tensioactive et étant ceux normalement utilisés au sein de bains galvaniques ayant des matrices formées par lesdits sels d'acide polycarboxylique organiques ; lesdits tensioactifs étant utilisés dans une quantité jamais supérieure à 0,005 L/L d'une solution aqueuse à 10 % p/v de ceux-ci ;

lesdits autres métaux ayant une action lustrante sont sélectionnés parmi le groupe constitué de l'argent, du tellure, du bismuth, du fer, du zinc, de l'iridium, du rhénium, du vanadium, du molybdène, du tungstène, sous une forme leur permettant d'être solubles et stables dans les conditions de travail, en quantités entre 0,005 et 0,2 g/L d'élément en tant que tel ;

lesdits sels d'acide polycarboxylique ayant à la fois des caractéristiques de tampon et un pouvoir de complexation, éventuellement en combinaison avec les acides correspondants pour la création du tampon opportun, ces acides et les sels respectifs sont chacun utilisés dans une quantité allant de 30 à 150 g/L ;

caractérisé en ce que du cyanure n'est pas présent dans la matrice du bain et sa teneur dans la solution galvanique s'explique par sa fonction de contre-ion dans les sels d'or seuls.

2. Bain galvanique selon la revendication 1, dans lequel lesdits sels d'or sont sélectionnés parmi : le dicyanoaurate de potassium, le tétracyanoaurate de potassium, le cyanoaurate d'ammonium, ou une combinaison de ceux-ci ; lesdits sels de cuivre sont sélectionnés parmi : le sulfate, le phosphate, le pyrophosphate, le chlorure, ou d'autres sels qui sont stables dans les conditions de travail du bain lui-même, et lesdits sels d'indium sont sélectionnés parmi le chlorure, le sulfate, le citrate, le tartrate, le gluconate, ou un complexe organique ou aminé.

3. Bain galvanique selon la revendication 2, dans lequel la quantité d'or va de 0,7 à 4 g/L, de préférence de 1,5 à 3 g/L, la quantité de cuivre est entre 0,3 et 2,5 g/L, de préférence entre 0,5 et 2 g/L. 5
4. Bain galvanique selon l'une quelconque des revendications 1 à 3, dans lequel lesdits sels d'acide polycarboxylique sont sélectionnés parmi : les citrates, les tartrates, les maléates, les malonates, éventuellement en combinaison avec les acides correspondants pour la création du tampon approprié, et éventuellement dans un mélange de leurs mélanges, et de préférence dans des quantités entre 50 et 100 g/L. 10
5. Bain galvanique selon l'une quelconque des revendications 1 à 4, dans lequel lesdites amines sont la triéthylènetétramine et la diéthylènetétramine, de préférence dans des quantités qui varient de 0,1 à 0,7 g/L. 15
6. Bain galvanique selon l'une quelconque des revendications 1 à 5, dans lequel lesdits autres métaux sont utilisés dans des quantités entre 0,010 et 0,1 g/L. 20
7. Bains galvaniques selon les revendications 1 à 6, dans lesquels lesdits composés sulfurés sont présents dans des quantités entre 0,01 et 0,500 g/L, et plus particulièrement dans des quantités entre 0,05 et 0,200 g/L. 25
8. Procédé galvanique pour le placage d'objets avec des alliages d'or de 12 à 18 carats, dans lequel les bains selon les revendications 1 à 7 sont utilisés. 30
9. Procédé galvanique selon la revendication 8, dans lequel ledit procédé est effectué dans une plage de pH entre 7 et 12, à une température entre 50 °C et 70 °C, et avec un courant appliqué entre 0,5 et 3 A/cm². 35
- 40
- 45
- 50
- 55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4358351 A [0007]
- US 4487664 A [0007]
- US 5085744 A [0007]
- US 4687557 A [0007]
- WO 2009037180 A [0007]