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(54) CYANIDE-FREE ELECTROLYTE FOR GALVANIC DEPOSITION OF GOLD ALLOYS

CYANIDFREIES ELEKTROLYT ZUR GALVANISCHEN ABSCHIEDUNG VON GOLDLEGIERUNGEN

ÉLECTROLYTE EXEMPT DE CYANURE POUR DÉPÔT GALVANIQUE D'ALLIAGES D'OR

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Description

[0001] The invention relates to a cyanide-free electrolyte for galvanic deposition of gold alloys, which has a neutral or alkaline aqueous solution of at least one gold complex and a complex of an alloy former for gold, the complexes being present in anionic form.

The electrolyte according to the invention is used in galvanic deposition, in particular in coatings made of gold alloys.

[0002] The galvanic deposition of gold has been effected for many years using electrolytes based on gold-cyanide complexes. In the alkaline range, proportions of toxic alkali cyanides are present and also the remaining metal cyanides are extremely toxic. In the acidic or neutral range, the cyanide released during electrolysis can escape in the form of toxic hydrogen cyanide or cyanogen. This toxicity and problematic handling associated therewith represents one of the substantial disadvantages of cyanide-containing electrolytes. A further problem relates to disposal of the cyanides contained in the depleted electrolyte.

[0003] Hence attempts have been made for some time to make available galvanic baths which dispense with the use of cyanides completely.

[0004] In this respect, galvanic baths based on gold-sulphite complexes are known. Thus US 4,435,253 teaches a galvanic bath which contains an alkali metal or ammonium-gold-sulphite and also, as further additives, thallium, which is toxic, and a carboxylic acid. The disadvantage of galvanic baths which contain gold-sulphite complexes is however their low stability so that the result is formation of colloidal metallic gold in the galvanic bath, as a result of which the electrolyte becomes unusable.

[0005] Galvanic baths in which the gold is present as thiosulphate complex are known from EP 0 611 840 A1. For stabilisation of these complexes, a sulphinate is added here since these baths also have problems with respect to the stability of the complexes. A further disadvantage in the just-mentioned galvanic baths concerns the fact that the current densities which can be applied are limited here since decomposition takes place at high current densities. Furthermore, the result with galvanic baths of this type can be odour problems.

[0006] In US 6,165,342, electrolysis baths for deposition of gold and gold alloys are presented, in which gold complexes with mercapto sulphonic acids and disulphide disulphonic acids are used. These compounds have the disadvantage that, because of the high molar weight of the sulphonic acids and the excess acid functions to be neutralised, they have a high proportion of extraneous material and hence only low gold contents. This fact also leads to corresponding processing and disposal problems.

[0007] US 2004/069641 A1 and US 6,733,651 B1 disclose a non-cyanogen type electrolytic solution for plating pure gold comprising a gold-complexing agent.

[0008] US 6,251,249 discloses a iodide-free and cyanide-free aqueous solution for deposition of precious metals, like e.g. gold, comprising an organosulfur compound or carboxylic acid complexing agent.

[0009] US 3,238,488 discloses a cyanide-free solution for electroplating metals like tin, copper, cadmium or zinc comprising a thioglycerol complexing agent.

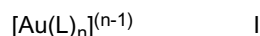
[0010] EP 1 300 488 A2 discloses a plating bath for plating metals like copper comprising organic compounds that increase the life of the plating bath and improve the efficiency of the plating process.

[0011] JP 2003/171789 discloses a cyanide-free gold-tin alloy plating bath comprising a sulfurous complexing agent for complexing gold and a carboxylic or polyamine complexing agent for complexing tin.

[0012] Starting herefrom, it was the object of the present invention to provide cyanide-free galvanic baths, the electrolyte of which has high stability and handling of which is substantially improved with respect to operating safety and environmental compatibility, relative to the galvanic baths known from the state of the art.

[0013] This object is achieved by the cyanide-free electrolytes for galvanic deposition of gold alloys having the features of claim 1. The further dependent claims reveal advantageous developments. In claim 17, a use according to the invention is cited.

[0014] According to the invention, a cyanide-free electrolyte for galvanic deposition of gold alloys from a neutral or alkaline aqueous solution is provided, comprising at least one anionic complex of the general formula I



with

L is selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butanetriol, mercapto-i-butanetriol, mercaptopentane-tetrol, cysteamine or combinations hereof, and

n = 2 to 5, preferably n = 2 to 4

and at least one anionic complex of the general formula II $[\text{M}(\text{L})_m]^{x-}$ II

with

M = alloy former for gold selected from the group comprising Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr and Pb,

L is selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butanetriol, mercapto-i-butanetriol, mercaptopentane-tetrol, cysteamine or combinations hereof, and $m = 2$ to 6 and $x = 1$ to 4, characterised in that the electrolyte comprises at least one brightener.

[0015] The gold is thereby present in the anionic complex in the oxidation state +1.

[0016] The electrolyte according to the invention leads to an entire series of important technological, ecological and economic advantages.

[0017] Thus with the electrolyte according to the invention, both matt, semi-glossy and glossy coatings with excellent quality can be produced.

[0018] The ligands used according to the invention (e.g. racemic 1-thioglycerine or cysteamine) are easy to handle, in particular with respect to transport, storage, metering and disposal. Furthermore, these ligands are miscible without limitation with water. The aqueous solutions are colourless, practically odour-free because of the low vapour pressure and stable thermally and in light and air within a wide temperature range (-30 to +100°C). The same applies to the anionic complexes formed therefrom with gold and metals M. They are also extremely readily watersoluble and in particular stable and odour-free in the preferred alkaline aqueous solutions in the temperature range +20 to +85°C. The ligands according to the invention thereby have a low molecular weight, e.g. thioglycerine 108 g/mol or cysteamine 77 g/mol, so that the gold contents of their complexes are very high (above 50%), which implies a low extraneous material ballast. The stability of the complexes is assisted further by the presence of excess ligand concentrations because this counteracts the reverse dissociation of the complexes. It is further advantageous that the same ligand can be used for a plurality of metals, which facilitates the deposition of alloys.

[0019] The cyanide-containing electrolytes known from the prior art can no longer be tolerated by the legislator without onerous conditions with respect to worker safety, storage and disposal for medical and ecological reasons due to the toxicity of the hydrogen cyanide and of the cyanides. The toxicity of the inventive ligands L is in contrast low. Thus thioglycerine and cysteamine are used for example partially even in the pharmaceutical and cosmetic field without hesitation. The use of the inventive electrolyte in galvanic equipments can thereby represent in many respects great progress.

[0020] According to the invention, the ligand L is selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butane-triol, mercapto-i-butanetriol, mercaptopentane-tetrol, cysteamine or combinations hereof. In particular thioglycerol is distinguished in that it is colourless and essentially odour-free. It forms soluble complexes with gold but also with copper, tin, indium, silver, iron, palladium, bismuth, zinc, cobalt, nickel, cadmium, gallium, germanium and antimony. A further advantage resides in the fact that thioglycerol is very easy to handle.

[0021] The new invented electrolyte can contain an excess of ligand for improving the stability of the various metal complexes depending on ion strength, pH or anodic oxidation. For gold, the number n of ligand is usually 4 but an excess of ligand at least added in the make-up of the first electrolyte gives a better convenient plating maintenance. The additional number of ligand can vary from 0 to 10.

[0022] The alloy former for gold is selected from the group consisting of copper, silver, iron, ruthenium, indium, gallium, germanium, tin, palladium, antimony, bismuth, cobalt, rhodium, iridium, nickel, zinc, cadmium, zirconium and lead. These metals are preferably present in the following oxidation states in the complexes: Cu(I) or Cu(II), Ag(I), Fe(II) or Fe(III), In(III), Ga(III), Ge(IV), Sn(II) or Sn(IV), Pd(II), Sb(III) or Sb(V), Bi(III) or Bi(V), Co(II), Ni(II), Zn(II), Cd(II), Ru(III), Rh(III), Ir(III), Ir(IV), Zr(IV), Pb(II).

[0023] The electrolyte comprises, as counterion for the anionic complex, preferably at least one cation E selected from the group consisting of alkali ions, in particular Na^+ and K^+ , quaternary ions, in particular NH_4^+ , NR_4^+ , PR_4^+ with $\text{R} = \text{C}_1\text{-C}_{12}$ alkyl or aryl, or diazolium ions and combinations hereof.

[0024] In addition to the previously-mentioned components, the electrolyte can comprise further complex formers. There are included herein in particular ethylenediaminetetraacetate, nitrilotriacetate, oxalate, carboxylates, ammonia, tartrate or 8-oxyquinoline and also mixtures hereof. These can also act as conductivity additives and as buffers.

[0025] For deposition of alloys, complexes of the further metals with the ligand L are added to the electrolyte.

[0026] The metal content of the electrolyte for gold as for each individual further metal present in the electrolyte is preferably in the range of 0.1 to 50 g/l electrolyte, in particular of 0.1 to 15 g/l electrolyte.

[0027] It is furthermore possible that the electrolyte comprises further supplements or additives. There are included herein in particular wetting agents, conducting salts and mixtures hereof.

[0028] The brightener is comprised preferably in a concentration of 0.001 to 5 g/l in the electrolyte. As brighteners there are suitable inorganic brighteners, in particular selenium or tellurium compounds, or organic brighteners, in particular pyridine-3-sulphonic acid, benzaldehyde, 2-butan-1,4-diol and/or sodium nicotinate, amines and polyamines: Amines and reaction products between amine and chloro derivatives (epichlorohydrin, dichlorodiethylether, chloro-bromo propane), e.g. condensation product of N, N'-bis{3-(dimethylamino)propyl} urea on dichlorodiethyl ether, polyethylene-imine and derivatives (oxidized or ethylenated), e.g. polyethylene-imine of molecular weight lower than 1000, aldehydes and ketones, sulfonated or solubilised by solvent or hydrotrope, e.g. anisaldehyde, vanillin, piperonal, benzyliden acetone, aryl sulfonates, e.g. para toluene benzene sulfonate, benzene sulfonate, naphthalene disulfonate acetylenic derivatives,

e.g. butynediol ethylenic derivates, e.g. allyl sulfonate, pyridine derivatives, e.g. sodium pyridin propane sulfonate or sodium benzyl pyridine carboxylate, amino acid + polypeptides: Peptone.

[0029] The wetting agent is preferably comprised in a concentration of 0.001 to 5 g/l in the electrolyte. For particular preference, the concentration is in the range of 0.2 to 2 g/l. The wetting agent is thereby preferably selected from the group of cationic, anionic, non-ionic or amphoteric surfactants.

[0030] Cationic surfactants include for example tetraalkylammonium halides, alkyltrimethylammonium halides, hydroxyethylalkylimidazolines, polyoxyethylenealkylmethylammonium halides, alkyl dimethylammonium halides, alkyl dimethylbenzylammonium halides, alkylamine hydrochlorides, alkylamine acetates, alkylamine oleates, alkylaminoethylglycines and alkylpyridinium halides.

[0031] There are included in the anionic surfactants e.g. alkyl- β -naphthalene sulphonic acids or salts thereof, saponified fats, alkylsulphonates, α -olefin sulphonates, alkylbenzene sulphonates, alkyl naphthalene sulphonates, alkyl diphenylether disulphonates, alkylether sulphonates, alkylsulphuric acid esters, polyoxyethylenealkylether sulphuric acid esters, polyoxyethylenealkylphenolether sulphuric acid esters, phosphoric acid monoesters of higher alcohols, polyoxyalkylenealkylether phosphoric acids and esters thereof, polyoxyalkylenealkylphenyl ether phosphates, polyoxyalkylenephenylether phosphates, polyoxyethylenealkylether phosphates, polyoxyethylenealkylether acetates, alkanoylsarcosines, alkanoidesarconisates, alkanoylmethylalanine salts, alkylsulphoacetates, acylmethyltaurines, alkyl fatty acid glycerine sulphuric acid esters, alkylsulphocarboxylesters, alkylsulphosuccinates, dialkylsulphosuccinates, alkyl polyoxyethylenesulphosuccinates and sodium succinic acid monooleylamides.

[0032] As non-ionic surfactants there are used e.g. polyoxyalkylenealkyl ethers or esters, polyoxyalkylene phenylethers, polyoxyalkylenenaphthyl (or alkyl naphthyl) ethers, polyoxyalkylenebisphenolethers, polyoxyethylene-polyoxypropylene block copolymers, polyoxyalkylenesorbitan fatty acid esters, polyoxyalkylenesorbitol fatty acid esters, polyethylene glycol fatty acid esters, polyoxyalkylene glycerine fatty acid esters, polyoxyalkylenealkylamines, polyoxyalkylene condensates of ethylene diamine, polyoxyalkylenealkylphenylformalin condensates, glycerine fatty acid esters, polyglycerine fatty acid esters, pentaerythritol fatty acid esters, sorbitan mono fatty acid esters, higher fatty acid monoethanolamides, alkylalkylolamides and oxyethylenealkylamines.

[0033] The amphoteric surfactants are preferably selected from the group consisting of 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaines, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinium betaines, 2-alkyl-N-carboxymethyl-N-carboxymethyloxyethylimidazolinium betaines, 2-alkyl-N-carboxyethyl-N-carboxymethyloxyethylimidazolinium betaines, N-alkyl- β -amino propionic acid or sodium salts thereof, alkylaminoethylglycine, N-alkyl-N-methyl-p-alanines or sodium salts thereof and fatty acid amidopropyl dimethylaminoacetic acid betaines.

[0034] The electrolyte preferably comprises at least one conducting salt in a concentration of 0.01 to 250 g/l, in particular 0.01 to 100 g/l or 0.01 to 50 g/l. There are thereby used as conducting salts preferably inorganic conducting salts, in particular from the group of sulphates, phosphates and pyrophosphates, or organic conducting salts, in particular from the group of salts of weak organic acids like formic, citric or acetic acid or preferably sodium citrate. The conducting salt thereby serves to reduce the voltage with appropriate current density. During the electrolysis on the anode, it must thereby have sufficient stability.

[0035] The electrolyte preferably has a pH value in the range of 7 to 14, in particular of 10 to 13. In order to adjust the pH value of the electrolyte, a caustic solution, in particular NaOH, is thereby preferably used.

[0036] The inventive electrolyte is preferably free of chlorides, as a result of which formation of chlorine and resulting products in the galvanic bath can be avoided.

[0037] The inventive electrolyte is preferably thermally stable in the range of 20 to 85°C so that it can be used in standard temperature conditions of galvanic baths.

[0038] Preferably, the number of ligands L of the complexes contained in the electrolyte corresponds at least to the sum of the coordination numbers of gold and also to the metals which are present. It is thereby preferred that an excess of ligands is present relative of the stoichiometrically fixed number of ligands for complete coordination of all metals, including gold. As a result, an improvement in the solubility and stability of the electrolyte can be ensured.

[0039] The inventive electrolyte is used for the deposition of coatings made of gold alloys.

[0040] At first, the inventive electrolyte can be used for flash plating of layers with a thickness of 0.03 μm to 0.5 μm . Similarly, the inventive electrolyte can be used for thick plating of layers with a thickness of 0.05 μm to 20 μm . Moreover, the present invention allows the electroforming of layers with a thickness of 20 μm to 500 μm .

[0041] The subject according to the invention is intended to be explained in more detail with reference to the subsequent examples without wishing to restrict said subject to the special embodiments represented here.

Example 1

Cyanide-free electrolyte for galvanic gold plating

[0042] 425 mg tetrachloroauric acid trihydrate $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (50% Au) is dissolved at room temperature in 45 ml

distilled water. With agitation, 0.50 ml 1-thioglycerine ($C_3H_8O_2S$, racemic, 98%, $d = 1.25 \text{ g cm}^{-3}$) is added in drops and the mixture is further agitated until a colourless suspension which reacts strongly acidic is produced. This suspension is treated with a solution of 0.225 g sodium hydroxide NaOH in 5 ml water, a clear colourless solution being produced showing approx. pH 10. This solution (50 ml, pH 13) with a content of 4.2 g l^{-1} gold (Au) is stable over at least 10 days in air in the temperature range 20 - 80°C, colourless and odour-free and can be used directly or with additives for galvanic gold deposition on various substrates. Well tested electrolyte additives are secondary potassium phosphate K_2HPO_4 , sodium-potassium-tartrate $NaKC_4H_6O_6$, tetrasodium ethylenediaminetetraacetate $Na_4C_{10}H_8N_2O_8$ (Na_4EDTA) and others. The thus produced electrolyte, without or with additives, also represents a suitable original or storage solution for the galvanic deposition of gold alloys. For this purpose, there are admixed therewith corresponding proportions of original solutions of the desired other alloy components.

Example 2

Cyanide- and chloride-free electrolyte for galvanic gold plating

[0043] 420 mg tetrachloroauric acid trihydrate $HAuCl_4 \cdot 3H_2O$ (50% Au) is dissolved in 50 ml distilled water and the obtained solution is mixed at 23°C in drops with agitation with 0.37 ml 1-thioglycerine ($C_3H_8O_2S$, racemic, 98%, $d = 1.25 \text{ g cm}^{-3}$). The thus obtained colourless suspension is further agitated at 40° for 30 minutes, allowed to settle and filtered. The precipitate of gold-(I)-thioglycerolate is washed with distilled water and alcohol and air-dried. There remain 275 mg of a yellow product which is suspended in 30 ml water and is treated therein at approx. 50°C with agitation with 0.28 ml 1-thioglycerine ($C_3H_8O_2S$, racemic, 98%, $d = 1.25 \text{ g cm}^{-3}$) and 0.12 g sodium hydroxide NaOH. A clear, colourless and odour-free solution is produced (pH 12, approx. 5.7 g l^{-1} Au) which can be used directly or with additives (cf. Example 1) for galvanic gold deposition on various substrates. This electrolyte likewise represents a suitable original or storage solution for the galvanic deposition of gold alloys. For this purpose, there are admixed therewith corresponding proportions of original solutions of the desired other alloy components.

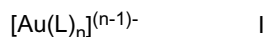
Example 3

Galvanic deposition of a gold-indium alloy

[0044] An electrolyte for gold-indium alloy has been made up with 2 g/L of gold thioglycerol and 0.4 g/L of indium thioglycerol. 100 g/L of sodium formiate gave the needed electrical conductivity while the pH was stabilized at 11 with potassium hydroxide. An anode of platinated titanium and a stirring agitation allows to pass 1.5 A/dm^2 at 50°C without burning at high current density. The deposit is bright enough up to $1 \text{ } \mu\text{m}$ plated in 10 min. The alloy composition is Au 80% and In 20%. The colour of the deposit in L, a, b values according Minolta colorimeter values is 85.0, 1,29 and 11,49, respectively, close to the 1N or 2N color.

Claims

1. Cyanide-free electrolyte for galvanic deposition of gold alloys comprising a neutral or alkaline aqueous solution of at least one anionic complex of the general formula I



with

L selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butanetriol, mercapto-i-butanetriol, mercaptopentane-tetrol, cysteamine or combinations hereof, and $n = 2$ to 5 and at least one anionic complex of the general formula II



with

M = alloy former for gold selected from the group comprising Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr and Pb,

L selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butanetriol, mercapto-i-butanetriol, mercaptopentane-tetrol, cysteamine or combinations hereof, and $m = 2$ to 6 and $x = 1$ to 4,

characterised in that the electrolyte comprises at least one brightener.

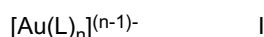
2. Electrolyte according to claim 1,
characterised in that the electrolyte contains, as counterion for the anionic complex, at least one cation E selected from the group comprising alkali ions, in particular Na^+ and K^+ , quaternary ions, in particular NH_4^+ , NR_4^+ , PR_4^+ with $\text{R} = \text{C}_1\text{-C}_{12}\text{-alkyl}$ or aryl, or diazoliun ions and combinations hereof.
3. Electrolyte according to one of the preceding claims,
characterised in that the electrolyte contains further complex formers, in particular ethylenediaminetetraacetate, nitrilotriacetate, ammonium tartrate or 8-oxyquinoline.
4. Electrolyte according to one of the preceding claims,
characterised in that the metal content of the electrolyte for each individual metal is in the range of 0.1 to 50 g/l electrolyte, in particular of 0.1 to 15 g/l electrolyte.
5. Electrolyte according to one of the preceding claims,
characterised in that the electrolyte comprises as further additives wetting agents, conducting salts or mixtures hereof.
6. Electrolyte according to claim 5,
characterised in that the at least one brightener is comprised in a concentration of 0.001 to 5 g/l in the electrolyte.
7. Electrolyte according to claim 5 or 6,
characterised in that an inorganic brightener is comprised as brightener, in particular a selenium and/or tellurium compound, or an organic brightener, in particular pyridine-3-sulphonic acid, benzaldehyde, 2-butan-1,4-diol and/or sodium nicotinate.
8. Electrolyte according to one of the claims 5 to 7,
characterised in that the at least one wetting agent is comprised in a concentration of 0.001 to 5 g/l, in particular of 0.2 to 2 g/l in the electrolyte.
9. Electrolyte according to one of the claims 5 to 8,
characterised in that the wetting agent is selected from the group of cationic, anionic, non-ionic, amphoteric surfactants or mixtures hereof.
10. Electrolyte according to one of the claims 5 to 9,
characterised in that the at least one conducting salt is comprised in a concentration of 0.01 to 250 g/l, in particular 0.01 to 100 g/l.
11. Electrolyte according to one of the claims 5 to 10,
characterised in that the at least one conducting salt is an inorganic conducting salt, in particular from the group of sulphates, phosphates and pyrophosphates, or an organic conducting salt, in particular from the group of salts of weak organic acids, preferably formic, citric or acetic acid.
12. Electrolyte according to one of the preceding claims,
characterised in that the pH value of the electrolyte is in the range of 7 to 14, in particular of 10 to 13.
13. Electrolyte according to one of the preceding claims,
characterised in that the electrolyte is free of chlorides.
14. Electrolyte according to one of the preceding claims,
characterised in that the electrolyte is thermally stable in the range of 20 to 85°C.
15. Electrolyte according to one of the preceding claims,
characterised in that the number of ligands L of the complexes comprised in the electrolyte corresponds at least to the sum of the maximum coordination numbers of gold and also of the metals present.
16. Electrolyte according to one of the preceding claims,
characterised in that the electrolyte is produced by dissolving at least one gold salt, at least one complex former L selected from the group of the anions of 1- and 2-thioglycerine, monothioglycol, mercapto-n-butanetriol, mercapto-

i-butanetriol, mercaptopentantetrol, cysteamine or combinations hereof, an ammonium- or alkali-containing caustic solution and a salt of an alloy former for gold selected from the group comprising Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr and Pb.

17. Use of the electrolyte according to one of the preceding claims for deposition of coatings made of gold alloys.
18. Use according to the preceding claim for flash plating of layers with a thickness of 0.03 μm to 0.5 μm , for thick plating of layers with a thickness of 0.05 μm to 20 μm or for electroforming of layers with a thickness of 20 μm to 500 μm .

Patentansprüche

1. Cyanidfreier Elektrolyt zur galvanischen Abscheidung von Goldlegierungen enthaltend eine neutrale oder eine alkalische wässrige Lösung von mindestens einem anionischen Komplex der allgemeinen Formel I



mit

L ausgewählt aus der Gruppe der Anionen von 1- und 2-Thioglycerin, Monothioglycol, Mercapto-n-butantriol, Mercapto-iso-butantriol, Mercaptopentantetrol, Cysteamin oder Kombinationen hiervon, und $n = 2$ bis 5 und mindestens einem anionischen Komplex der allgemeinen Formel II



mit

M= Legierungsbildner für Gold ausgewählt aus der Gruppe umfassend Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr und Pb,

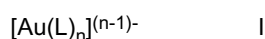
L ausgewählt aus der Gruppe der Anionen von 1- und 2-Thioglycerin, Monothioglycol, Mercapto-n-butantriol, Mercapto-i-butantriol, Mercaptopentantetrol, Cysteamin oder Kombinationen hiervon, und $m = 2$ bis 6 und $x = 1$ bis 4, **dadurch gekennzeichnet, dass** der Elektrolyt mindestens einen optischen Aufheller beinhaltet.

2. Elektrolyt gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Elektrolyt als Gegenion zu dem anionischen Komplex mindestens ein Kation E enthält, ausgewählt aus der Gruppe umfassend Alkaliionen, insbesondere Na^+ und K^+ , quaternäre Ionen, insbesondere NH_4^+ , NR_4^+ , PR_4^+ mit $\text{R} = \text{C}_1\text{-C}_{12}\text{-Alkyl}$ oder Aryl, oder Diazonium-Ionen und Kombinationen hiervon.
3. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Elektrolyt weitere Komplexbildner, insbesondere Ethylendiamintetraacetat, Nitrilotriacetat, Ammoniak, Tartrat oder 8-Oxychinolin, enthält.
4. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Metallgehalt des Elektrolytes für jedes einzelne Metall im Bereich von 0,1 bis 50 g/L Elektrolyt, insbesondere 0,1 bis 15 g/L Elektrolyt liegt.
5. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Elektrolyt als weitere Additive Benetzungsreagenzien, leitfähige Salze oder Mischungen hiervon enthält.
6. Elektrolyt gemäß Anspruch 5, **dadurch gekennzeichnet, dass** der mindestens eine optische Aufheller in einer Konzentration von 0,001 bis 5 g/L in dem Elektrolyt enthalten ist.
7. Elektrolyt gemäß Anspruch 5 oder 6, **dadurch gekennzeichnet, dass** ein anorganischer optischer Aufheller als optischer Aufheller enthalten ist, insbesondere eine Selen- oder Tellur-Verbindung, oder ein organischer optischer Aufheller, insbesondere Pyridin-3-Schwefelsäure, Benzaldehyd, 2-Butin-1,4-diol und/oder Natriumnicotinat.
8. Elektrolyt gemäß einem der Ansprüche 5 bis 7, **dadurch gekennzeichnet, dass** das mindestens eine Benetzungsreagenz in einer Konzentration von 0,001 bis 5 g/L, insbesondere von 0,2 bis 2 g/L in dem Elektrolyt enthalten ist.

9. Elektrolyt gemäß einem der Ansprüche 5 bis 8, **dadurch gekennzeichnet, dass** das Benetzungsreagenz aus der Gruppe der Kationen, Anionen, Nicht-Ionen, amphoteren Beschichtungsreagenzien oder aus Mischungen hiervon ausgewählt ist.
10. Elektrolyt gemäß einem der Ansprüche 5 bis 8, **dadurch gekennzeichnet, dass** das mindestens eine leitfähige Salz in einer Konzentration von 0,01 bis 250 g/L, insbesondere von 0,01 bis 100 g/L enthalten ist.
11. Elektrolyt gemäß einem der Ansprüche 5 bis 8, **dadurch gekennzeichnet, dass** das mindestens eine leitfähige Salz ein anorganisches leitfähiges Salz ist, insbesondere ausgewählt aus der Gruppe der Sulfate, Phosphate und Pyrophosphate, oder ein organisches leitfähiges Salz, insbesondere ausgewählt aus der Gruppe der Salze schwacher organischer Säuren, bevorzugt Ameisen-, Zitronen- oder Essigsäure.
12. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der pH-Wert des Elektrolyts im Bereich von 7 bis 14, insbesondere von 10 bis 13 liegt.
13. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Elektrolyt frei von Chloriden ist.
14. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Elektrolyt im Bereich von 20 bis 85°C thermisch stabil ist.
15. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Anzahl der Liganden L der in dem Elektrolyt enthaltenen Komplexe mindestens der Summe der maximalen Koordinationszahl von Gold und auch von den anwesenden Metallen entspricht.
16. Elektrolyt gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Elektrolyt durch Lösen von mindestens einem Goldsalz, mindestens einem Komplex bei dem L vorher aus der Gruppe der Anionen von 1- und 2-Thioglycerin, Monothioglycol, Mercapto-n-butantriol, Mercapto-i-butantriol, Mercaptopentantetrol, Cysteamin oder Kombinationen hiervon ausgewählt wurde, einer Ammonium oder Alkali-haltigen Ätzlösung und einem Salz eines Legierungsbildners für Gold ausgewählt aus der Gruppe von Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr und Pb, hergestellt wird.
17. Verwendung des Elektrolyts gemäß einem der vorhergehenden Ansprüche für die Abscheidung von Beschichtungen auf Basis von Goldlegierungen.
18. Verwendung des Elektrolyts gemäß dem vorhergehenden Anspruch für die Vorbeschichtung von Schichten mit einer Dicke von 0,03 µm bis 0,05 µm, für die Dicklagenbeschichtung von Schichten mit einer Dicke von 0,05 µm bis 20 µm oder für die Galvanoformung von Schichten mit einer Dicke von 20 µm bis 500 µm.

Revendications

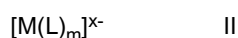
1. Électrolyte sans cyanure pour le dépôt galvanique d'alliages d'or comprenant une solution aqueuse neutre ou alcalins d'au moins un complexe anionique de formule générale I



dans laquelle

L est choisi dans le groupe constitué par les anions de 1- et 2-thioglycérine, de monothioglycol, de mercapto-n-butanetriol, de mercapto-i-butanetriol, de mercaptopentantetrol, de cystéamine ou leurs combinaisons, et n = 2 à 5,

et d'au moins un complexe anionique de formule générale II



dans laquelle

M = agent de formation d'alliage pour l'or choisi dans le groupe comprenant Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr et Pb,

L est choisi dans le groupe constitué par les anions de 1- et 2-thioglycérine, de monothioglycol, de mercapto-n-butanetriol, de mercapto-i-butanetriol, de mercaptopentananetétrol, de cystéamine ou leurs combinaisons, et $m = 2$ à 6 et $x = 1$ à 4,

caractérisé en ce que l'électrolyte comprend au moins un azurant optique.

2. Électrolyte selon la revendication 1, **caractérisé en ce que** l'électrolyte contient, en tant que contre-ion pour le complexe anionique, au moins un cation E choisi dans le groupe comprenant les ions alcalins, en particulier Na^+ et K^+ , les ions quaternaires, en particulier NH_4^+ , NR_4^+ , PR_4^+ avec R = alkyle en C_1 - C_{12} ou aryle, ou les ions diazolum et leurs combinaisons.
3. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'électrolyte contient en outre des agents de formation de complexes, en particulier le tétraacétate d'éthylène diamine, le nitrilotriacétate, le tartrate d'ammonium ou la 8-oxyquinoline.
4. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la teneur en métal de l'électrolyte pour chaque métal individuel est dans la plage allant de 0,1 à 50 g/l d'électrolyte, en particulier de 0,1 à 15 g/l d'électrolyte.
5. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'électrolyte comprend en tant qu'additifs supplémentaires des agents mouillants, des sels conducteurs ou leurs mélanges.
6. Électrolyte selon la revendication 5, **caractérisé en ce que** ledit au moins un azurant optique est compris en une concentration de 0,001 à 5 g/l dans l'électrolyte.
7. Électrolyte selon la revendication 5 ou 6, **caractérisé en ce qu'un** azurant optique inorganique est compris en tant qu'azurant optique, en particulier un composé de sélénium et/ou de tellure, ou un azurant optique organique, en particulier l'acide pyridine-3-sulfonique, le benzaldéhyde, le 2-butyne-1,4-diol et/ou le nicotinate de sodium.
8. Électrolyte selon l'une quelconque des revendications 5 à 7, **caractérisé en ce que** ledit au moins un agent mouillant est compris en une concentration de 0,001 à 5 g/l, en particulier de 0,2 à 2 g/l, dans l'électrolyte.
9. Électrolyte selon l'une quelconque des revendications 5 à 8, **caractérisé en ce que** l'agent mouillant est choisi dans le groupe constitué par les tensioactifs cationiques, anioniques, non ioniques, amphotères ou leurs mélanges.
10. Électrolyte selon l'une quelconque des revendications 5 à 9, **caractérisé en ce que** ledit au moins un sel conducteur est compris en une concentration de 0,01 à 250 g/l, en particulier de 0,01 à 100 g/l.
11. Électrolyte selon l'une quelconque des revendications 5 à 10, **caractérisé en ce que** ledit au moins un sel conducteur est un sel conducteur inorganique, en particulier du groupe des sulfates, des phosphates et des pyrophosphates, ou un sel conducteur organique, en particulier du groupe des sels d'acides organiques faibles, de préférence l'acide formique, citrique ou acétique.
12. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le pH de l'électrolyte est dans la plage allant de 7 à 14, en particulier de 10 à 13.
13. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'électrolyte est exempt de chlorures.
14. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'électrolyte est thermiquement stable dans la plage allant de 20 à 85 °C.
15. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le nombre de ligands L des complexes compris dans l'électrolyte correspond au moins à la somme des nombres de coordination maximums de l'or et également des métaux présents.
16. Électrolyte selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'électrolyte est produit par dissolution d'au moins un sel d'or, d'au moins un agent de formation de complexes L choisi dans le groupe constitué par les anions de 1- et 2-thioglycérine, de monothioglycol, de mercapto-n-butanetriol, de mercapto-i-

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butanetriol, de mercaptopentantétrol, de cystéamine ou leurs combinaisons, une solution caustique contenant de l'ammonium ou un alcali, et un sel d'un agent de formation d'alliages pour l'or choisi dans le groupe comprenant Cu, Ag, Fe, Ru, In, Ga, Ge, Sn, Pd, Sb, Bi, Co, Rh, Ir, Ni, Zn, Cd, Zr et Pb.

- 5 **17.** Utilisation de l'électrolyte selon l'une quelconque des revendications précédentes pour le dépôt de revêtements en alliages d'or.
- 10 **18.** Utilisation selon la revendication précédente pour le placage flash de couches d'une épaisseur de 0,03 μm à 0,5 μm , pour le placage épais de couches d'une épaisseur de 0,05 μm à 20 μm , ou pour l'électroformage de couches d'une épaisseur de 20 μm à 500 μm .

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REFERENCES CITED IN THE DESCRIPTION

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